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Materials Balance for Benzene: Level II

JRB Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC

May 80

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Toxic Substances
Washington, DC 20460

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EPA

Materials Balance for Benzene

Level II

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16. ABSTRACT

A Level II materials balance was performed on benzene. Data are reported for benzene production from petroleum by four processes (catalytic reformation, toluene dealkylation, toluene disproportionation, and isolation from pyrolysis gasoline) and for production from coal during coking. Amounts of benzene consumed for the synthesis of eight direct derivatives (ethylbenzene, cumene, cyclohexane, nitrobenzene, maleic anhydride, mono- and dichlorobenzene, alkylbenzenes, and biphenyl) and exports are presented. These uses constitute approximately 99 percent of total benzene usage. Non-consumptive uses (solvents and pesticide component) are also tabulated. Releases due to each of the above processes are reported or estimated where possible using published and unpublished data. In addition, releases due to indirect production (refinery operation, coke oven operations, oil spills, non-ferrous metals manufacturing, ore mining, wood processing, coal mining, and two phases of the textile industry) are presented. Production of benzene as a component of gasoline and releases due to all phases of gasoline use are estimated. Locations of sites with high levels of benzene releases due to production and use are tabulated: the major "hotspots" are Baton Rouge, Louisiana; Houston/Galveston, Texas; Midland, Michigan; and Puerto Rico. The uncertainty ranges of all numbers used or derived in this report are evaluated when possible and tabulated. Data gaps are evaluated and general recommendations are presented. The results of the report are summarized in two figures: the Environmental Flow Diagram for benzene in Appendix A, and the Materials Balance Flow Diagram in the Executive Summary.

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FINAL REPORT

LEVEL II MATERIALS BALANCE

BENZENE

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
SURVEY AND ANALYSIS DIVISION
Task No. 21
Contract No. 68-01-5793
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Submitted: December 8, 1980

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ABSTRACT

A Level II materials balance was performed on benzene. Data are reported for benzene production from petroleum by four processes (catalytic reformation, toluene dealkylation, toluene disproportionation, and isolation from pyrolysis gasoline) and for production from coal during coking. Amounts of benzene consumed for the synthesis of eight direct derivatives (ethylbenzene, cumene, cyclohexane, nitrobenzene, maleic anhydride, mono- and dichlorobenzene, alkylbenzenes, and biphenyl) and exports are presented. These uses constitute approximately 99 percent of total benzene usage. Nonconsumptive uses (solvents and pesticide component) are also tabulated. Releases due to each of the above processes are reported or estimated where possible using published and unpublished data. In addition, releases due to indirect production (refinery operation, coke oven operations, oil spills, non-ferrous metals manufacturing, ore mining, wood processing, coal mining, and two phases of the textile industry) are presented. Production of benzene as a component of gasoline and releases due to all phases of gasoline use are estimated. Locations of sites with high levels of benzene releases due to production and use are tabulated: the major "hotspots" are Baton Rouge, Louisiana; Houston/Galveston, Texas; Midland, Michigan; and Puerto Rico. The uncertainty ranges of all numbers used or derived in this report are evaluated when possible and tabulated. Data gaps are evaluated and general recommendations are presented. The results of the report are summarized in two figures: the Environmental Flow Diagram for benzene in Appendix A, and the Materials Balance Diagram in the Executive Summary.

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EXECUTIVE SUMMARY

This Level II materials balance on benzene was performed in response to Task Order No. 21 under Contract No. 68-01-5793 with Survey and Analysis Division, Office of Pesticides and Toxic Substances, EPA.

The Materials Balance Summary Diagram for benzene is included at the end of this Executive Summary. It shows only those processes for which data were obtainable. The more comprehensive Environmental Flow Diagram for benzene appears as Appendix A of the report. All data refer to the year 1978 unless otherwise stated.

DIRECT PRODUCTION

Benzene is obtained by the fractionation and enrichment of fossil fuels. It is produced from petroleum by four processes:

1. Catalytic reformation of the naphtha petroleum fraction;
2. Dealkylation of toluene;
3. Disproportionation of toluene; and
4. Isolation from pyrolysis gasoline as a byproduct of ethylene manufacture.

Benzene is obtained from coal by extraction from the light oil formed during coking. This extraction may be done either at the coking plant or after sale of the light oil to refineries. The contribution by each process and the total production of benzene from petroleum are shown below:

	Benzene Produced, 1978	
Process	(kkg)	(% of Total)
Catalytic reformation	2,360,000	48
Toluene dealkylation	1,300,000	26
Toluene disproportionation	121,000	2
Pyrolysis gasoline	925,000	19
Petroleum Subtotal	4,710,000	95
Extraction of light oil by coking plants	178,000	4
Extraction of light oil by refineries or process unknown	74,000	1
Petroleum and Coal Total	4,960,000	100

Total benzene releases due to the four production processes (including storage and transport) were estimated to be 7,000 to 11,800 kkg. Of these releases, 6,400 to 11,200 kkg were estimated to go to air and 620 kkg to water. No estimate of releases to landfills was possible. The above values do not include benzene released during gasoline production by refineries.

Benzene releases due to benzene-producing coke oven operations could not be estimated.

INDIRECT PRODUCTION

Indirect sources of benzene production were also analyzed for benzene releases. Total estimated benzene releases were as follows: refinery operations, including gasoline production, 20,000 kkg to air, 1 kkg to water, and 228,000 kkg to landfills; coke oven operations, 3,000 to 59,000 kkg to air; and oil spills, 30 to 11,000 kkg to water. Releases from miscellaneous operations are listed on the Materials Balance Summary Diagram.

IMPORTS

Benzene imports amounted to 225,000 kkg in 1978. The estimated releases attributed to importing were 13 kkg to air and 13 kkg to water.

CONSUMPTIVE USES

The predominant use of benzene is as a starting material for the synthesis of other organic compounds. The eight major direct derivatives of benzene and their contributions to total benzene consumption are listed in Table ES-1.

A summary of the releases due to synthesis of each product is shown in Table ES-2.

EXPORTS

Exports accounted for 151,000 kkg of benzene in 1978. Estimated releases due to exportation (dockside loading) were 15 kkg to air, 2 kkg to water, and a negligible amount to land.

NONCONSUMPTIVE USES

Less than 5 percent of benzene production in 1978 was used nonconsumptively; that is, benzene was not coverted to another compound before use. The categories of nonconsumptive use and the estimated amounts used are as follows:

Use	Benzene Used (kkg)
Solvent	9,600
Pesticide	Unknown

Table ES-1 Summary of Consumptive Uses of Benzene

Product	Formed by Reacting Benzene with:	Secondary Products or Uses	Benzene Used, 1978 (kkg)	Consumptive Use (% of total)
Ethylbenzene	Ethylene	Styrene; polystyrene	2,810,000	54
Cumene	Propylene	Phenol	1,030,000	20
Cyclohexane	Hydrogen	Cyclohexanone; Nylon 66	836,000	16
Nitrobenzene	Nitric acid	Aniline	170,000	3
Chlorobenzenes	Chlorine	Chemical intermediates	134,000	3
Alkylbenzenes	10- to 14-Carbon alkyl chlorides	Detergents	132,000	3
Maleic anhydride	Oxidant	Chemical intermediates	111,000	2
Biphenyl	Itself (with heat)	PCBs; Dyes	7,000	0.1
			5,230,000	101.1*

*Totals do not add to 100% due to rounding.

Table ES-2 Releases of Benzene Due to Consumptive Uses (1978)

Product Synthesized	Estimated Releases (kkg) to: Air	Water	Land	Total	Percent of Total
Ethylbenzene	3,900	120	NK*	4,000	36
Cumene	2,000	40	NK	2,000	18
Cyclohexane	290	~0	NK	290	3
Nitrobenzene	340	16	NK	360	3
Maleic Anhydride	3,600	8	~0	3,600	33
Chlorobenzenes	340	16	NK	360	3
Alkylbenzenes	170	35	NK	200	2
Biphenyl	41	NK	NK	41	0.4
TOTALS	11,000	240	NK	11,000	

*NK = Not known

Solvent use of benzene has decreased since the 1977 OSHA Emergency Benzene Standard and the 1977 ban on use of benzene in consumer goods by the Consumer Products Safety Commission. Releases due to solvent use in 1978 were estimated to be 1,500 kkg to air, 1,500 kkg to water, and an unknown amount to land.

The inventory of benzene as of January 1, 1979, was 272,000 kkg less than on January 1, 1978. This decrease in inventory is treated as increased supply when benzene sources and sinks are balanced.

BENZENE AS A FUEL CONSTITUENT

The largest single source of benzene releases stems from its presence as a minor component of gasoline. The production of gasoline by refineries is a major indirect source of benzene, generating an estimated 4.44 x 10^6 kkg of benzene in 1979. Releases due to refining were included under indirect production with petroleum refining operations. Other sources of releases are listed below:

Process	Releases to air, 1979 (kkg)
Gasoline storage	4,700 - 6,700
Gasoline transport	4,600 - 8,200
Gasoline vending	1,200 - 6,100
Gasoline consumption	58,000 - 165,000
Sum for gasoline-powered automobiles, motorcycles, trucks and buses	69,000 - 186,000

The difference between the amount of benzene consumed in gasoline (4.44 x 10^6 kkg) and total benzene releases due to fuel use (1.9 x 10^5 kkg) was 4.3 x 10^6 kkg. This value represents the difference between benzene destroyed by combustion and that generated by combustion. Since the amount generated by combustion could not be estimated, this difference is reported as benzene destroyed.

Geographic distribution of benzene releases due to gasoline use are assumed to be directly related to population density. Data to confirm this assumption are available from the U.S. Department of Transportation, but were not received in time for inclusion in this report.

DISPOSAL/DESTRUCTION OF END PRODUCTS

No information was available to permit estimation of benzene releases due to incineration of benzene-containing end products. It was estimated that 760 kkg of benzene from refinery wastes were placed in landfills in 1978. It was not possible to estimate the distribution of this waste to water and air. In addition to benzene destroyed during gasoline combustion, an estimated 7,900 kkg were destroyed by emission controls during solvent use or refinery operations.

LOCATIONS OF MAJOR BENZENE RELEASE SITES

Tabulation of sites and estimated benzene releases at those sites indicated that the top five areas for potential benzene releases were Iberville Parish, Louisiana; Harris and Galveston counties, Texas; Midland, Michigan; and Puerto Rico. This tabulation does not include releases due to the presence of benzene in gasoline.

UNCERTAINTIES AND DATA GAPS

Whenever a basis for evaluation existed, an attempt was made to quantify the uncertainties of estimates. These uncertainties were expressed as a range of values or a percentage.

The following data gaps were encountered in performing this study:

1. Lack of information on benzene releases at coke ovens. A literature search and industry inquiries are recommended.
2. Lack of information on generation and disposal of benzene-containing solid residues, during production and consumptive uses. Industry inquiries are recommended.

SUMMARY OF RELEASES BY CATEGORY

The table below summarizes estimated releases by major category of production and uses.

	Estimated Releases (kkg)[1] to:			
Category	Air	Water	Land	Total
Production from petroleum	6,400-11,200	620	?	7,000-11,800
Production from coal	?	?	?	?
Imports	13	13	?	25
Indirect production	23,000-79,000	200-11,000	?	23,000-90,000
Consumptive uses	11,000	240	?	11,200
Nonconsumptive uses	1,500	1,500	?	3,000
Component of gasoline	69,000-186,000	?	?	69,000-186,000
SUMS:	111,000-290,000	2,000-13,000	?	113,000-302,000

1. A range of values is not meant to be a statistical range or set of error limits, but results from differing independent estimates of the releases.

SUMMARY: MATERIALS BALANCE FOR BENZENE

The diagram summarizes the data and estimates available at present for the materials balance for benzene. It shows a breakdown of the categories in the table above into individual processes. Operations for which no data were available were not included. The diagram also characterizes the uncertainties of the release estimates as described in the key below the diagram.

The "balance" equation for the materials balance is shown below. It was formulated by using the upper value in a range of values as follows:

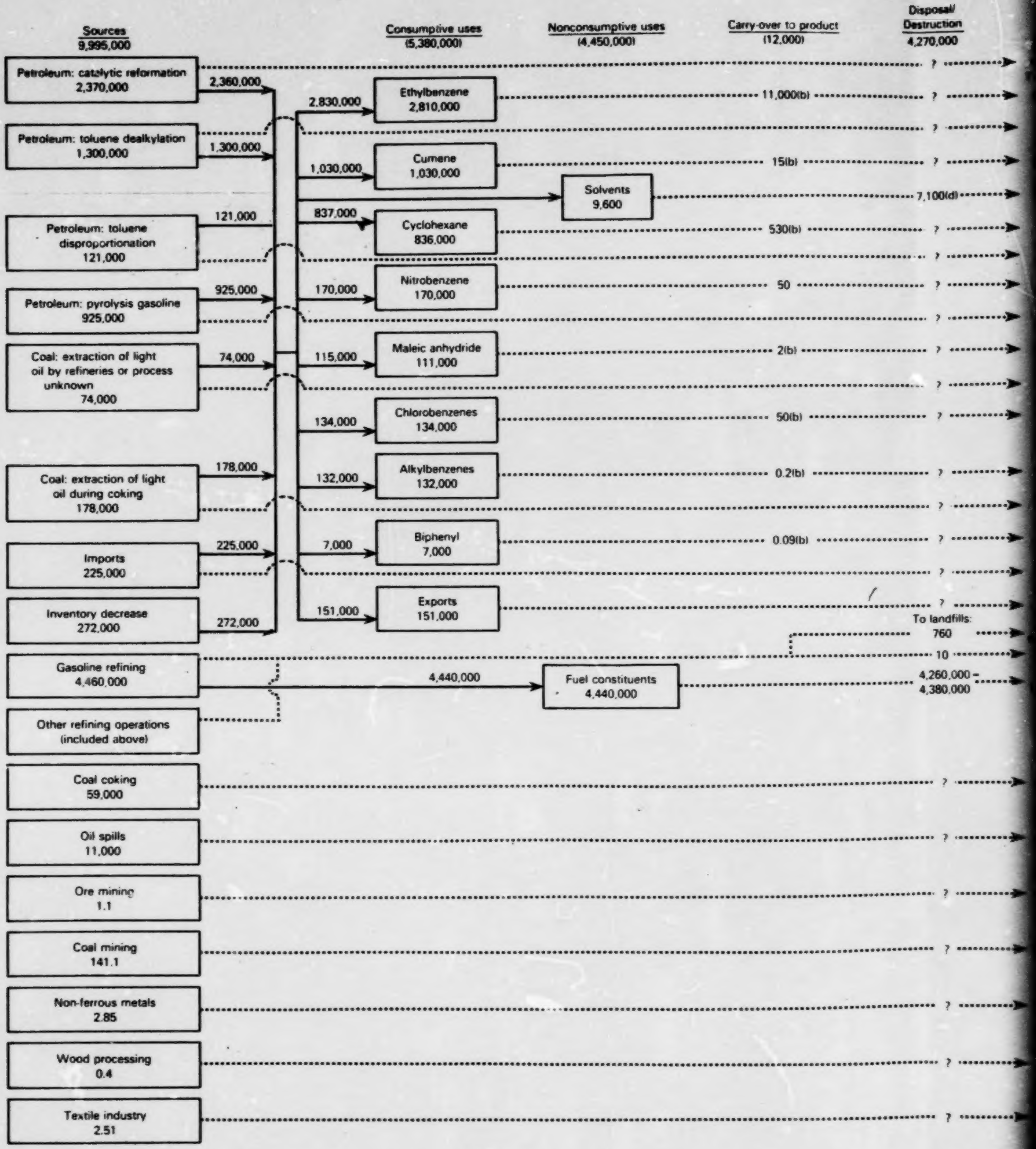
Benzene available = Benzene accounted for by uses + Losses + Storage

Production + Imports + Inventory Decrease = Consumptive uses + Exports + Carry-over + Disposal/Destruction + Releases

9,995,000 kkg = 5,380,000 kkg + 12,000 kkg + 4,270,000 kkg + 302,000 kkg

= 9,964,000

The apparent imbalance of 31,000 kkg (0.3 percent of available benzene) is probably explained by the fact that consumptive use amounts were calculated independently from direct production amounts. We believe that the apparent imbalance is within the uncertainty ranges of the respective totals.


Sources
9,995,000
Consumptive uses
(5,380,000)
Nonconsumptive uses
(4,450,000)
Carry-over to product
(12,000)
Disposal/Destruction
4,270,000
Petroleum: catalytic reformation
2,370,000
2,360,000
Petroleum: toluene dealkylation
1,300,000
1,300,000
Petroleum: toluene disproportionation
121,000
121,000
Petroleum: pyrolysis gasoline
925,000
925,000
Coal: extraction of light oil by refineries or process unknown
74,000
74,000
Coal: extraction of light oil during coking
178,000
178,000
Imports
225,000
225,000
Inventory decrease
272,000
272,000
Gasoline refining
4,460,000
Other refining operations (included above)
Coal coking
59,000
Oil spills
11,000
Ore mining
1.1
Coal mining
141.1
Non-ferrous metals
2.85
Wood processing
0.4
Textile industry
2.51
2,830,000
Ethylbenzene
2,810,000
11,000(b)
1,030,000
Cumene
1,030,000
15(b)
Solvents
9,600
7,100(d)
837,000
Cyclohexane
836,000
530(b)
170,000
Nitrobenzene
170,000
50
115,000
Maleic anhydride
111,000
2(b)
134,000
Chlorobenzenes
134,000
50(b)
132,000
Alkylbenzenes
132,000
0.2(b)
7,000
Biphenyl
7,000
0.09(b)
151,000
Exports
151,000
To landfills:
760
10
4,440,000
Fuel constituents
4,440,000
4,260,000 – 4,380,000
?

Included in catalytic reformation totals

KEY: a = ± a factor < 1; b = ± a factor of 2-10; c = ± a factor of > 10; d = no basis for evaluation of uncertainties

	RELEASES TO –			
Disposal/ Destruction 4,270,000	Air (288,000)	Water (13,600)	Land (?)	Totals (302,000)
?	6,400* 11,200	620*	?	7,000* 11,800(d)
?	3,900(d)	120(d)	?	4,000(d)
?	*	*	?	*
?	2,000(d)	40(d)	?	2,000(d)
7,100(d)	1,500(d)	1,500	?	3,000(d)
?	290(d)	0	?	290(d)
?	*	*	?	*
?	340(d)	16(d)	?	360(d)
?	*	*	*	*
?	3,600(d)	8(d)	~ 0(d)	3,600(d)
?	*	*	*	*
?	340(d)	16(d)	?	360(d)
?	170(d)	35(d)	?	210(d)
?	?	?	?	?
?	41(d)	?	?	41(d)
?	13(c)	13(c)	?	25(c)
?	15(d)	2(d)	?	17(d)
To landfills: 760	Not estimated	Not estimated	—	Not estimated
10	20,000(d)	1(c)		20,000
4,260,000 – 4,380,000	69,000 – 186,000(d)	?	?	69,000 – 186,000(d)
?	3,000 – 59,000(d)	?	?	3,000 – 59,000(d)
?	0	30 – 11,000(d)	?	30 – 11,000(d)
?	?	1.1(d)	?	1.1(d)
?	?	141.1(d)	?	141.1(d)
?	?	2.85(d)	?	2.85(d)
?	?	0.4(d)	?	0.4(d)
?	?	2.51(d)	?	2.51(d)

Figure ES-1: Materials Balance for Benzene, 1978 (k

3 P

1.0 INTRODUCTION

This Level II materials balance on benzene was prepared in response to a task order from Survey and Analysis Division, U.S. Environmental Protection Agency. The report is organized according to the processes during which benzene might be released to the environment (direct production, consumptive use, etc.).

In the tables and figures reporting release data and estimates, the term "releases to land" was defined as meaning "material applied to the soil," as opposed to material applied to a landfill. A landfill has been interpreted as a form of waste storage rather than as a sink. The rationale was that benzene-containing solids in a landfill would readily lose benzene by leaching or evaporation to yield water or air releases. Therefore, quantities of benzene-containing solids applied to a landfill would be apportioned to air and water to reflect long-term reality. On the other hand, actual "releases to land" would include use of pesticides, fertilizers, or other chemicals that would yield benzene due to microbial or photochemical degradation. Such releases would be tabulated as indirect production of benzene.

Data for certain sections of this report were provided by Versar, Inc., under directive of Monitoring and Data Support Division, U.S. Environmental Protection Agency. In particular, Versar data were used in the estimation of releases to water during consumptive uses.

1.1 PROPERTIES OF BENZENE

Benzene is a clear, flammable liquid with a pungent odor. Its physical properties are summarized below (Weast 1977-78; Strecher 1968):

Melting Point	5.5°C
Boiling Point	80.1°C
Density	0.87865 g/cc
Solubility in H_2O	0.70 g/l at 25°C
Temperature at which vapor pressure = 1 Torr	-36.7°C

Benzene's physical properties indicate a compound likely to be released to air or to evaporate to air from the surface of a biphasic water mixture. Benzene's density value has been used to convert volumes to kkg. No temperature correction was applied to the density value.

1.2 ENVIRONMENTAL FLOW DIAGRAM FOR BENZENE

Appendix A shows the environmental flow diagram for benzene. This diagram attempts to demonstrate as many as possible of the sources and uses of benzene, as well as potential points of release to the environment. It is not our purpose to discuss the diagram in detail in this report. It serves as a guide, however, in formulating the questions to be asked in this and other benzene materials balances.

2.0 DIRECT PRODUCTION OF BENZENE

Benzene is commercially produced by three routes: from petroleum by various methods; from coal during coke production; and from condensates from gas wells. While coal was the original commercial source of benzene, petroleum is the primary source of benzene today (Kirk-Othmer 1976). In 1978, according to the U.S. International Trade Commission (USITC), 178,000 kkg of benzene were obtained from coal while 4,780,000 kkg were derived from petroleum and gas well condensates. The flow of benzene through a refinery is affected by refinery product mix, types of crude processed, types of processes and equipment, the market, and market conditions for a specific refinery (Appendix B-1). Numerous industrial contacts indicated variation of these parameters not only between companies, but among the refineries of the same company as well.

As a result of the diverse sources of variation in benzene production, Chapters 2 and 3 are devoted to this process. Chapter 2 presents generalized models of the benzene production processes and the releases generated by these processes as estimated from numerous industry contacts and accessible literature. Chapter 3 presents information on other operations in a petroleum refinery that may be a source of benzene releases and other possible indirect sources of benzene releases.

2.1 PRODUCTION FROM PETROLEUM

Benzene is a component of crude oil in concentrations ranging from 0.001 to 0.4 percent (Versar 1977). Table 2.1 is a compilation of the available data on the concentration of benzene in crude oil. Recovery of benzene is uneconomical unless its concentration is increased by some catalytic or thermal reaction.

The four basic commercial methods used to increase the benzene concentration in petroleum and then isolate it are:

1. Catalytic reformation,
2. Dealkylation of toluene,
3. Disproportionation of toluene, and
4. Isolation from pyrolysis gasoline (Kirk-Othmer 1976).

These methods are listed in order of decreasing commercial significance. Process descriptions of these methods and the types and quantities of benzene releases generated are presented in Sections 2.1.3 through 2.1.6.

Some petroleum refineries also recover benzene from coal-derived light oil. This benzene is included in the total production from coal.

One refinery is known to produce small quantities of benzene from condensates recovered from gas wells. This benzene is included in the total production from petroleum.

Table 2.1 Available Data on the Percent of Benzene in Crude Oil

Source of Crude Oil	Benzene in crude oil (% by volume)	Reference
Pennsylvania	0.04	Leverson and Berry 1967
Bradford, Pennsylvania	0.06	Shreve and Norris
East Texas	0.07	Shreve and Norris
Ponca City, Oklahoma	0.15	Shreve and Norris
Worldwide range	0.001 to 0.4	Versar 1977
Estimated average	0.15	Mara and Lee 1978

2.1.1 Producers and Locations

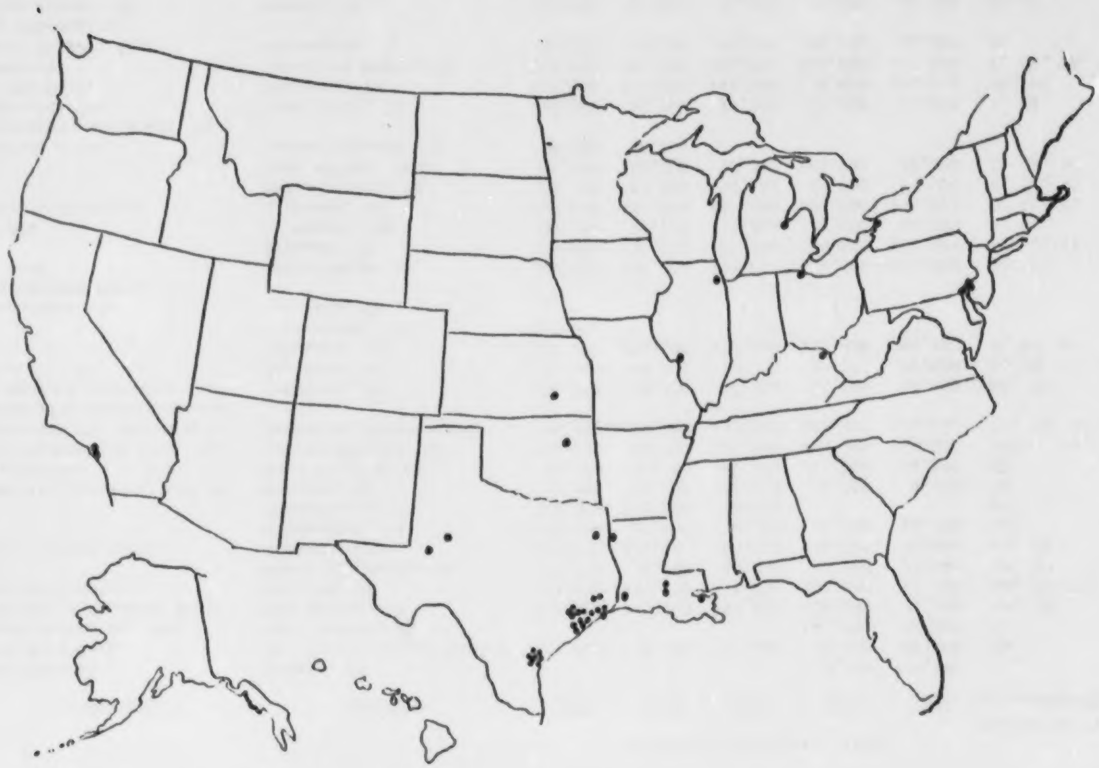
The map in Figure 2.1 shows the locations of U.S. plants producing benzene from petroleum. The majority of these are located on the Texas Gulf Coast, specifically in the Houston and Corpus Christi areas.

A compilation of the U.S. producers of benzene from petroleum, by type of process used, is presented in Table 2.2. Company names and locations were compiled from information contained in USITC publications, Versar (1979), Neufeld et al. (1978), and SRI (1977). Some plants were listed in the literature as using more than one process without indication of relative capacities. In these cases, plant capacity was assumed to be evenly distributed among the processes listed. No allocation was made to the process of recovering benzene from light oil unless specifically indicated in the literature. The final column of the table indicates whether the production was captively consumed and contacts the percentage of captive consumption.

2.1.2 Amounts Produced

The estimated production by each plant producing benzene from petroleum is also given in Table 2.2. The years 1975-1979 are included.

Estimated production (kkg) for a given refinery in a given year was calculated by using the following formula:



Locations

Unplotted - Channelview, TX; St. Croix, VI; Penuelas, PR; Guayama, PR; Alliance, LA; Taft, LA

Figure 2.1 Producers of Benzene from Petroleum, 1978

Table 2.2 Producers and Production, 1975-1979
(Sources: A.D. Little, Inc. 1977; SRI 1977; Versar 1979; Neufeld et al. 1978)

Company	Location	Estimated Production[1] (kkg) 1979	1978	1977	1976	1975	Production Processes[2] and Use
Allied Chemical	Winnie, TX				8,520	5,680	
Amerada Hess Corp.	St. Croix, Virgin Islands	162,000	146,000	159,000	71,000	47,400	CR
American Petrofina, Inc.	Port Arthur, TX				42,600	28,400	C
(Cosden Oil & Chemical Co.)	Big Spring, TX	144,000	130,000	142,000	128,000	85,300	CR, TD
Ashland Oil, Inc.	Ashland, KY	159,000	144,000	156,000	142,000	95,000	CR, TD, LO
	North Tonawanda, NY	57,200	51,700	56,200	42,600	28,400	CR, LO
Atlantic Richfield Co.	Houston, TX	139,000	126,000	103,000	125,000	83,400	CR, TP
	Wilmington, CA	29,800	27,000	29,300	34,100	22,700	CR
	Channelview, TX	162,000	146,000	78,200			PG
Charter International Oil Co.	Houston, TX	12,400	11,200	12,200	14,200	9,470	CR
Cities Service Co., Inc.	Lake Charles, LA	62,100	56,200	61,100	71,000	47,400	CR
Coastal States Gas Prod. Co.	Corpus Christi, TX	174,000	157,000	171,000	199,000	133,000	25% C, CR, TD
Commonwealth Oil Refining Co. (Commonwealth Petrochemicals)	Penuelas, Puerto Rico	460,000	416,000	452,000	525,000	350,000	PC, CR, TD, PG
Crown Central Petroleum Corp.	Pasadena, TX	57,200	51,700	56,200	65,300	43,600	CR, TD
Dow Chemical Co.	Bay City, MI	74,600	67,500	73,300	85,200	56,900	C, TD, PG, LO
	Freeport, TX	124,000	112,000	122,000	142,000	94,700	C, TD, PG
	Plaquemine, LA	149,000					
Eastman-Kodak Co. (Texas Eastman Div.)	Longview, TX	?	?	?	?	?	
Exxon Corp.	Baton Rouge, LA	174,000	157,000	171,000	185,000	123,000	CR, PG
	Baytown, TX	149,000	135,000	147,000	176,000	117,000	67% C, CR
Getty Oil	El Dorado, KS	32,300	29,200	31,800	37,000	24,600	C, CR
Gulf Oil Corporation	Alliance, LA	167,000	151,000	164,000	199,000	133,000	C, CR, TD
	Philadelphia, PA	92,000	83,200	90,400	93,700	62,500	C, CR, TD
	Port Arthur, TX	186,000	169,000	97,700	108,000	72,000	C, CR, PG
Kerr-McGee Corp. (Southwestern Oil & Ref. Co.)	Corpus Christi, TX	39,800	36,000				
Marathon Oil Co.	Texas City, TX	17,400	15,700	17,100	17,000	11,400	C, CR
Mobil Oil Corp.	Beaumont, TX	149,000	135,000	147,000	170,000	114,000	CR, PG
Monsanto Co.	Chocolate Bayou, TX	211,000	191,000	208,000	213,000	142,000	C, CR, TD, PG
Pennzoil United, Inc. (Atlas Processing)	Shreveport, LA	87,000	78,700	36,600	42,600	28,400	PG
Phillips Petrol. Co.	Sweeny, TX	24,900	22,500	24,400	62,500	41,700	C, CR
	Guayama, Puerto Rico	273,000	247,000	269,000	312,000	208,000	PC, CR, TD
Quintana-Howell	Corpus Christi, TX	224,000	202,000	17,100			CR

Table 2.2 Producers and Production, 1975-1979 (continued)

		Estimated Production[3] (kkg)					Production Processes[2] and Use
Company	Location	1979	1978	1977	1976	1975	
Shell Oil Co.	Deer Park, TX	298,000	270,000	220,000	213,000	142,000	C, CR, PG
	Odessa, TX	29,800	27,000	29,300	17,000	11,400	CR, TD
	Wood River, IL	112,000	101,000	110,000	114,000	76,000	CR, LO
Standard Oil Co. of Calif.	El Segundo, CA	57,200	51,700	56,200	65,300	43,600	C, CR
Standard Oil Co. (Ind.)(AMOCO)	Texas City, TX	211,000	191,000	208,000		161,000	C, CR
Standard Oil Co. (Ohio) (B.P. Oil Co.)	Marcus Hook, PA				22,700	15,200	
Sun Oil Co.	Marcus Hook, PA	72,100	65,200	70,800	42,600	28,400	CR, TP
	Corpus Christi, TX	94,500	85,400	92,800	99,400	66,300	C, CR, TD
	Tulsa, OK	59,700	54,000	58,600	68,200	45,500	CR, TP
	Toledo, OH	184,000	166,000	120,000			CR, TD
Tenneco, Inc.	Chalmette, LA	24,900	22,500	24,400	28,400	18,900	CR, LO
Texaco, Inc.	Port Arthur, TX	112,000	101,000	110,000	128,000	85,300	73% C, CR
	Westville, NJ	87,000	78,700	85,500	99,400	66,300	PC, CR
Union Carbide Corp.	Taft, LA	174,000	157,000	171,000	199,000	133,000	C, PG
Union Oil Co. of Calif.	Lemont, IL	42,300	38,200	41,500	54,000	36,000	CR, LO
Union Oil-American Petrofina	Beaumont, TX	54,700	49,500	53,700	54,000	36,000	50% C, TD
Union Pacific Corp. (Champlin Petroleum Co.)	Corpus Christi, TX	24,900	22,500	24,400	28,400	18,900	C, CR
TOTAL USITC PRODUCTION		5,430,000[3]	4,780,000	4,570,000	4,540,000	3,190,000	

1. Sources: A.D. Little, Inc., 1977; SRI, 1977; Versar, 1979; Neufeld *et al.*, 1978.

2. Key: C= captive use, PC= partially captive, CR= catalytic reformation, TD= toluene dealkylation, TP= toluene disproportionation, PG= pyrolysis gasoline, LO= light oil.

3. Derived from plant capacities and USITC production totals as described in Section 2.1.2.

4. Estimated by extrapolating USITC data for the months January through July, 1979.

$$\text{Estimated production} = \frac{\text{Total benzene production by petroleum refineries for year (USITC)}}{\text{Total U.S. plant capacity for year (SRI), minus capacity of plants not listed by USITC as producing benzene that year}} \times \text{Capacity of individual plant (SRI)}$$

The following points were considered in the application of the formula to derive benzene production figures:

1. The USITC production figures are in gallons; therefore, a conversion factor of 3.33×10^{-3} kkg/gal was applied to obtain production in kkg.
2. It was assumed that an individual plant's production was proportional to its capacity.
3. Estimates for 1979 were based on USITC data from January to July which were extrapolated for the remainder of the year.
4. Plant capacities for 1975-1976 were assumed to be equal to those for 1976 listed by Versar (1979).

2.1.3 Production by Catalytic Reformation

Catalytic reformation is the most commonly used of the four methods for producing benzene from petroleum. Of the 46 refineries listed as producers of benzene in 1978 (Table 2.2), 37 were reported to have the capacity to produce benzene by catalytic reformation.

The catalytic reformation method is composed of two distinct processes: reforming and separation. The purpose of the process is to increase the quantity of aromatic component of the selected crude petroleum fraction, usually a naphtha cut, by reforming the molecular structure of hydrocarbons or rearranging them. Appendix B-2 lists the types of feedstocks used in the catalytic reformation method of benzene production. The main chemical reactions involved are listed in Table 2.3. These reforming chemical reactions are accelerated by noble metal catalysts such as rhenium and platinum on a bed of silica and alumina in hydrogen under normal atmospheric to moderate pressures (Considine 1974; Industrial Sources 1980). A compilation of the industrial reforming processes and flow diagram are presented in Appendix B.

Table 2.3 Chemical Reactions in Reforming Hydrocarbons in a Naphtha Cut to Form Benzene

Chemical Reaction	Hydrocarbon Component Reformed
Dehydrogenation	Naphthenes
Dehydrocyclization	Paraffins
Isomerization	Paraffins
Hydrocracking heavy paraffins	Paraffins

(Source: Adapted from Considine (1974))

The purpose of the separation process is two-fold: separation of the aromatic from nonaromatic components, and fractionation of the aromatic mixture into specific components. The five commercial aromatic recovery methods, the feedstocks from which the aromatics are recovered, and their aromatic content are presented in Table 2.4. A detailed description of these processes is included in Appendix B-3.

Table 2.4 Methods of Aromatic Recovery from Petroleum[1]

Process	Feedstock	Percent Aromatic Content for Process Efficiency
Liquid-liquid extraction	Catalytic reformate	20-65
Extractive distillation	Pyrolysis gasoline	65-90
Azeotropic distillation	Pyrolysis gasoline	Above 90%
Absorption on solids	Coke oven gas	?
Crystallization by freezing	Unknown	Special cases for benzene

1. Adapted from Weissermel and Arpe (1978).

The liquid-liquid extraction method is the most frequently employed method. A table of the liquid-liquid extraction processes and solvents is also included in Appendix B. The liquid-liquid extraction processes used most often are the Udex and Sulfolane processes (Industrial Sources 1980).

2.1.3.1 Amounts Produced by Catalytic Reformation

Total capacity for benzene production by petroleum refineries are calculated as 7,080,000 kkg during 1978. Of this amount 3,500,000 kkg were estimated to be for the catalytic reformation process (SRI 1977; Neufeld et al. 1978). Of the total petroleum-derived benzene production (as opposed to capacity) of 4,780,000 kkg (USITC), 2,360,000 kkg were attributed to production by catalytic reformation. This value was calculated by assuming that 1978 production was proportional to capacity as follows:

$$\frac{\left(\begin{array}{c}\text{Total}\\ \text{Production}\\ \text{1978}\end{array}\right)\left(\begin{array}{c}\text{Capacity,}\\ \text{Catalytic}\\ \text{Reformation}\\ \text{Plants}\end{array}\right)}{\text{Total Benzene Capacity}} = \begin{array}{c}\text{Production,}\\ \text{Catalytic Reformation}\\ \text{1978}\end{array}$$

Catalytic reformation capacity of plants is presented in Table 2.2.

2.1.3.2 Releases Due to Catalytic Reformation

The two steps in catalytic reformation, reforming and separation, will be examined individually in an effort to elucidate the quantities and types of benzene releases for this method of benzene production.

Within the reformation step, there are seven major and a few minor proprietary processes in use today. The "platforming" process is in greatest commercial use, with more than 500 units in operation (Hydrocarbon Processing 1978). Assuming that the relative proportions of these reforming proprietary processes are the same for benzene production as they are for the catalytic reforming industry, the "platforming" process is the most widely used process. Therefore, the following sources of releases are based on the platforming process; releases for this process will be assumed to be typical of benzene releases from reforming in the benzene industry. Appendix B-4 contains flow diagrams and details of the "platforming" process. These are three production process steps during which benzene may be released: catalyst regeneration and replacement; hydrogen gas regeneration; and extraction of the light gases. For more detailed information on these releases refer to Appendix B.

A review of the pertinent literature and contacts with industry did not reveal any release factors, nor were data obtained to calculate releases for these processes. Contacts with industry did indicate that benzene releases from these processes would probably be in the form of vapors with concentrations in the parts-per-million range. As a result of these discussions, JRB estimates that two aspects of these processes deserve further investigation: light gases collected at the separator may contain greater benzene concentrations, and catalyst regeneration at the vendor's site may result in possible worker exposure to benzene.

Of the five aromatic recovery methods, liquid-liquid extraction is the method used to recover aromatics from reformate. There are nine proprietary processes for liquid-liquid extraction in use today. The "Sulfolane" and "Udex" processes are the major processes in use, as indicated by numerous industrial contacts. Refer to Appendix B-3 for details on the types of liquid-liquid extraction processes and flow diagrams. The following sources of releases are for the Sulfolane and Udex processes, assumed to be representative of benzene releases for the extraction process.

Benzene releases may be associated with certain steps in or products resulting from the aromatic extraction processes: solvent regeneration or reconstitution, raffinate wash water, and raffinate. For more detailed information on these releases refer to Appendix B-3.

A review of the literature and industry contacts did not reveal any release factors nor were data available to calculate releases from all these sources. However, the reviewed literature did indicate that benzene recoveries of 99.9 percent are not unusual for the Sulfolane process (Hydrocarbon Processing 1978). The remaining 0.1 percent of benzene is estimated by JRB to be found in one - or, more likely, a combination - of the following: raffinate, raffinate wash water, or the remaining solvent. Assuming the other extraction processes have similar efficiencies, the amount of benzene that was released to these sources was calculated as follows:

$$\left(\begin{array}{c}\text{Benzene Produced}\\ \text{by Catalytic}\\ \text{Reformation, 1978}\end{array}\right)\left(\begin{array}{c}\text{Fraction}\\ \text{not}\\ \text{Recovered}\end{array}\right) = \begin{array}{c}\text{Maximum Possible}\\ \text{Releases During}\\ \text{Extraction}\end{array}$$

$$(2{,}360{,}000\ \text{kkg}) \quad (0.001) = 2{,}360\ \text{kkg}$$

Due to the great variability of the extraction process, refinery operations, and market demand, we estimated the accuracy of the quantity of benzene not covered in the extraction process to be +500%, -50%.

This benzene would be distributed among raffinate, raffinate wash water, and solvent. The estimated distribution of benzene released in the solvent extraction process is presented in Table 2.5 below.

The reviewed literature revealed two estimates for the quantity of benzene released during the catalytic reformation process. These estimates are presented in Table 2.6. The sources that provided these estimates did not state any uncertainties nor was information given from which uncertainties could be calculated. Refer to Section 2.1.7 for general estimates of benzene releases from petroleum-derived benzene production.

2.1.4 Production of Benzene by Dealkylation

The method that produces the second largest quantity of benzene from petroleum is dealkylation of toluene and higher alkylaromatics. Of the 43 refineries believed to produce benzene in 1978 for which we

Table 2.5 Estimated Distribution of Benzene Not Recovered by the Extraction Process

Benzene Containing Liquid	Unrecovered Benzene (%)	(kkg)	Disposition of Liquid
Solvent	2	50	Recycled, rarely disposed
Raffinate Wash Water	60	1400	Recycled, eventually sent to refinery effluent treatment facility
Raffinate	38	900	A. Blended into gasoline or jet fuel B. Used for olefin production C. Unknown

Table 2.6 Benzene Releases Due to the Production of Benzene by the Catalytic Reformation Method

Source of Estimate	Release Factor	Background Information	Release Calculations
Walker 1976	1 percent of the benzene produced by catalytic reformation	Walker estimated that this is a maximum factor.	(2,360,000 kkg benzene produced in 1978 by catalytic reformation) x (1 x 10^{-2} kkg/kkg) = 20,000 kkg benzene released (maximum)
Ochner et al. 1979	67,000 kg/yr/refinery	The estimate by T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio. An estimate of the total quantity of benzene releases from catalytic reformation process in 1976 was divided by the number of facilities producing benzene by the catalytic reformation process to arrive at a release factor.	(67 kkg/yr/refinery) x 37 refineries using the catalytic reformation = 2,500 kkg of benzene released.

have data on production methods, 15 were reported to have the capacity to produce benzene by dealkylation (Table 2.2).

Dealkylation normally occurs in a hydrogen environment; therefore, the method is called hydrodealkylation. There are two commercial processes for hydrodealkylation: catalytic and thermal. Refer to Appendix B-5 for the proprietary names and descriptions of these processes. Frequency of use of the processes is about equal, and process steps are very similar (Kirk-Othmer 1976). In both, toluene is heated and then charged to a reactor in the presence of excess hydrogen. Toluene reacts with the hydrogen to produce benzene and methane gas. The reaction product is separated, stabilized, and distilled to recover benzene. The major differences between the two processes are that toluene is heated to a higher temperature in the thermal process, and a catalyst is present in the catalytic process (Kirk-Othmer 1976).

In a newer method, steam dealkylation, toluene is reacted with steam to produce benzene, carbon monoxide, carbon dioxide, and hydrogen. The advantage is that hydrogen is produced rather than consumed (Kirk-Othmer 1976).

A list of feedstocks and the chemical reactions in the production of benzene by the dealkylation methods is presented in Table 2.7.

Table 2.7 Feedstock and Chemical Reactions for the Dealkylation Method of Benzene Production

Feedstock[1]	Frequency of Use	Chemical Reaction[2]
92-95% Toluene	Usual feedstock	Demethylation
85-90% Toluene	Less frequently used	Demethylation, Dealkylation
Longer chain alkyl chains: heavy catalytic reformates, catalytic oils	Much less than the first two feedstocks	Combination of demethylation and dealkylation

1. SRI 1977.

2. PEDCo 1977.

The amount of benzene produced by toluene dealkylation varies depending upon the demand for benzene and relative prices of benzene and toluene. Due to fluctuating market conditions and high cost of manufactured feedstock (compared to the other benzene feedstocks) the dealkylation method is generally used by petrochemical refinery complexes with excess toluene not needed for gasoline blending. Further, the benzene produced in this way is generally used for in-house consumption (Industrial Sources 1980).

As a result of the decrease in lead levels in gasoline, toluene is now blended in greater quantities into gasoline to increase the octane rating. Because of the sharp increase in demand for unleaded gasoline, JRB estimates that the quantity of benzene produced by hydrodealkylation of toluene will significantly decrease.

2.1.4.1 Amounts of Benzene Produced by Dealkylation

Estimated capacity for benzene production by toluene dealkylation was 1,920,000 kkg for 1978 (SRI 1977; Neufeld et al. 1978). Production was estimated at 1,300,000 kkg; this estimate was derived from USITC production data for petroleum-derived benzene using the formula in Section 2.1.3.1.

Information on refinery complexes have toluene dealkylation capacity is presented in Table 2.2.

2.1.4.2 Releases Due to the Dealkylation Method of Benzene Production

The two different processes for toluene dealkylation produce different quantities of releases. Table 2.8 presents a list of the potential releases from the dealkylation method.

Ochner et al. (1976) reported a release factor of 88 kkg of benzene per year per producer for the dealkylation method. The release factor was derived from an estimation of the total benzene released as a result of the alkylation method for 1976. This estimate was made by private communication with T. W. Hughes, Monsanto Research Corporation. The total estimate was divided by the number of facilities producing benzene by the dealkylation method to arrive at the release factor. The total releases of benzene from the dealkylation method for 1978 are calculated below.

$$\begin{pmatrix}\text{Release}\\ \text{Factor}\\ \text{Per User}\end{pmatrix} \quad (\text{Users}) \quad = \quad \begin{matrix}\text{Benzene Released}\\ \text{from Dealkylation}\\ 1978\end{matrix}$$

$$(88 \text{ kkg/yr}) \quad (15) \quad = \quad 1300 \text{ kkg}$$

No uncertainties were given with the release factor nor were data provided from which uncertainties could be determined. However, JRB estimated that the uncertainty would be very high (+500%, -200%) due to the variation in processes, equipment, process flow, and quantities of benzene produced by each of the 15 users of the dealkylation method. Refer to Section 2.1.7 for general estimates of benzene releaes from petroleum-derived benzene production.

2.1.5 Production of Benzene by Transalkylation and Disproportionation

Transalkylation and disproportionation of toluene is the method that produces the third largest quantity of benzene, although it ranks last in number of plants using it. Of the 43 refineries thought to produce benzene in 1978 for which we had data on production methods, only three had the capacity to produce benzene by toluene disproportionation (Table 2.2).

Table 2.8 Process Releases from the Dealkylation Method

Source	Form of Release
Separation of benzene and methane	Vapors contaminating methane
Distillation	Vapors
Regeneration of catalyst in the catalytic method	Vapors probably in ppm concentrations which occur every 2000-4000 hours depending on severity of operating conditions
CO_2 and H_2 during dealkylation	Vapors in gases and steam condensates

The synthesis of benzene by this method is the result of a realkylation of alkylaromatics. This occurs by two types of reactions: disproportionation and transalkylation. An explanation of these reactions is presented in the table below.

Table 2.9 Difference Between Disproportionation and Transalkylation

Reaction	Explanation
Disproportionation	Conversion of alkylaromatics into equal parts of higher and lower alkylaromatics or, in some instances, dealkylated aromatics.
Transalkylation	Transfer of alkyl groups from higher to lower alkylated aromatics.

A description of the process, proprietary names, and a process flow diagram are located in Appendix B.

The feedstock for this method is toluene and C^9 aromatics. JRB estimates that as the demand for toluene due to its use as a gasoline component increases, the use of this method and the quantity produced will decrease.

2.1.5.1 Amounts Produced by Transalkylation and Disproportionation

Estimated capacity for benzene production by toluene disproportionation was 180,000 kkg for 1978 (SRI 1977; Neufeld et al. 1978). The actual production was estimated at 121,000 kkg, as calculated from USITC data and capacity information as described in Section 2.1.3.1.

Information on plants having toluene disproportionation capacity is presented in Table 2.2.

2.1.5.2 Releases of Benzene Due to the Transalkylation and Disproportionation Method

Benzene releases differ slightly for the three proprietary processes for this method. Table 2.10 presents a general list of the process releases from the transalkylation and disproportionation method. Ochner et al. (1976) presented a release factor of 20 kkg of benzene per year per producer by transalkylation and disproportionation. This estimate was derived as described in Section 2.1.4.2. The total releases of benzene from this method are calculated below.

Table 2.10 Potential Sources of Benzene Releases from the Transalkylation-Disproportionation Method

Process Source	Estimated Form of Release
Separation of benzene and xylene	Liquid - contamination of xylene
Regeneration of the catalyst	Vapors - probably in concentrations in the ppm range
Heavy hydrocarbons that do not break down	Solid - may be contaminated with benzene

$$\begin{pmatrix}\text{Release}\\ \text{Factor}\\ \text{per User}\end{pmatrix} \quad (\text{Users}) \quad = \quad \begin{matrix}\text{Benzene Release}\\ \text{from Transalkylation-}\\ \text{Disproportionation}\\ \text{Method, 1978}\end{matrix}$$

$$(20\ \text{kkg/yr}) \quad (3) \quad = \quad 60\ \text{kkg}$$

No uncertainty or data to compute an uncertainty were reported for the release factor. JRB estimated the uncertainty to be +50%, -20% due to the similarities of the proprietary processes and small number of users. Refer to Section 2.1.7 for general estimates of benzene releases from petroleum-derived benzene production.

2.1.6 Production of Benzene from Pyrolysis Gasoline

The smallest quantity of benzene from petroleum was produced by this method. JRB estimated that as the demand for auto fuel increases so will the quantity of benzene produced from pyrolysis gasoline. First, benzene, toluene, and xylene may be produced as byproducts of auto fuel produced from pyrolysis gasoline. Second, toluene demand will increase due to its use as an auto fuel additive; the resulting decrease in availability or rise in cost will therefore limit toluene use as a benzene feedstock for the dealkylation and transalkylation-disproportionation methods.

Of the 43 refineries believed to produce benzene in 1978 for which we also had data on production methods, 11 were reported to have the capacity to produce benzene from pyrolysis gasoline.

Pyrolysis gasoline is a byproduct of the steam cracking of heavy naphthas or gas oils in the production of ethylene. Refer to Appendix B for a list of feedstocks. Pyrolysis gasoline has a high content of unsaturated aliphatic and aromatic hydrocarbons that are used as feedstock in the production of aromatics and gasoline (Kirk-Othmer 1976). There are several proprietary processes; two of these, IFP and Pyrotol, are described accompanied by process flow diagrams in Appendix B.

2.1.6.1 Amounts of Benzene Produced from Pyrolysis Gasoline

Estimated capacity for benzene production from pyrolysis gasoline was 1,320,000 kkg for 1978 (SRI 1977; Neufeld et al. 1978). Production for 1978 was estimated at 925,000 kkg from USITC data as described in Section 2.1.3.1.

Information on facilities with capacity for production from pyrolysis gasoline is presented in Table 2.2.

Table 2.11 lists the feedstocks and quantities of benzene produced from them.

Table 2.11 Pyrolysis Gasoline Feedstocks and Quantities of Benzene Produced from Each Type

Ethylene Feedstocks	Estimated Benzene Produced
Lower Paraffins	
Ethane	Not an economical feedstock
Propane	45 kg of propane or
n-Butane	n-Butane produce 2.3 to 4.6 kg of benzene
Heavier Hydrocarbons	
Naphthas	45 kg of naphthas
Gas Oil	gas oils, or condensates are estimated to produce 6 to 11 kg of benzene
Condensates	

(Source: SRI 1977; JRB-derived estimates from SRI data)

2.1.6.2 Releases Due to the Pyrolysis Gasoline Method of Benzene Production

The two proprietary processes for pyrolysis gasoline have different environmental releases (Appendix B). Table 2.12 lists the potential releases from the pyrolysis gasoline processes.

Ochner et al. (1976) reported a release factor of 60 kkg of benzene per year per producer by the pyrolysis gasoline method. The release factor was obtained as described in Section 2.1.4.2. The total benzene released for three plants in 1978 was 180 kkg. The release factor was reported without estimates of uncertainties, nor were data available to calculate uncertainties. JRB estimated that uncertainties would be high (+300%, -100%) because of possible variation in the feedstock composition and the number of plants using the process.

2.1.7 General Releases Due to Petroleum-Derived Benzene Production

Total releases of benzene from the four petroleum production methods were estimated to be 4,000 kkg for 1978; Table 2.13 lists those due to each method. Other release factors based on a percentage of the total production are given in Table 2.14. There is a wide range between these estimates: 30 to 50,000 kkg/year. JRB estimated overall benzene releases from petroleum production of benzene to be closer to the 4,000 kkg/yr figure than to the more extreme values in Table 2.14. This conclusion was based on the judgment that for economic reasons, all feasible control methods would be implemented to prevent undue loss of a product. This evaluation was qualitatively confirmed by several industrial contacts.

Table 2.12 Generalized List of Potential Benzene Releases from Pyrolysis Gasoline Processes

Process Type[1] and Release Source	Probable Form of Release
IFP	
1. Gum	1. Nonoxidative removal of gums from catalyst probably every 3 to 6 months. Solids and vapors probably contain some benzene.
2. Catalyst Regeneration	2. Oxidation of coke deposits on catalyst every 9 to 12 months may release benzene vapors in the ppm range.
3. Distillation Process	3. Liquid contamination of condensates and reaction products.
Pyrotol	
1. Gum removal from evaporator	1. Benzene in gums, probably in solid waste
2. Desulfurization	2. Benzene contamination of sulfur extracted from the feedstock, probably in solid waste.
3. Clay treatment process	3. Clay contains contaminants strained from benzene; contaminants could contain benzene which would be disposed of as solid waste.

[1] See Appendix B for process descriptions.

Table 2.13 Summary of Estimated Benzene Releases for the Four Petroleum Production Processes

Process	Estimated Benzene Releases (kkg)	Section
Catalytic reformation	2,500	2.1.3.2
Dealkylation	1,300	2.1.4.2
Transalkylation - disproportionation	60	2.1.5.2
Pyrolysis Gasoline	180	2.1.6.2
TOTAL	4,000	

(Source: Ochner et al. 1979)

A release factor for benzene releases to air was reported by PEDCo (1977). This factor, 1.8×10^{-5} kkg/kkg produced, was based on a Union Carbide estimate for a single facility thought to be using the pyrolysis gasoline production method. The factor was judged to be not credible in magnitude and not applicable to refineries in general, and it was not used further in this report.

A release factor for water (Versar 1977) of 1.3×10^{-4} kkg/kkg produced, was based on an average of 0.22 percent of benzene lost to the environment, as reported by an industrial survey. It was assumed that 6 percent of the total benzene released went to water. This factor yielded an estimate of 620 kkg of benzene released to water.

In estimating the uncertainties of the releases to water during benzene production, two factors were taken into account: the wide range for industrial estimates of percentage of benzene lost to the environment (these estimates differ by a factor of 730); and the allocation of 6 percent of total losses to water. Based on these two factors, an uncertainty of ± a factor of 1,000 was assigned to the estimate of benzene releases to water.

The solid wastes generated from benzene production include the following types: solid, liquid-solid slurries, and sludges. The components of the solid wastes that appear to come directly from the benzene synthesis processes are acid and alkali sludges (Saxton and Markus-Kramer 1975).

The quantity of solid waste generated from benzene production was calculated using data of Saxton and Markus-Kramer (1975), who calculated the amount of solid was generated from benzene production in 1972. These

Table 2.14 Summary of the Estimated Overall Benzene Releases During Production from Petroleum

Source of Release Factor	Release Factor	Calculation of Benzene Releases	Benzene Released (kkg)
Walker 1976	1 percent of benzene produced	(1%) (4,780,000 kkg produced in 1978) =	50,000
Patterson et al. 1976	0.5 percent of benzene produced	(0.5%) (4,780,000 kkg produced in 1978) =	20,000
Versar 1977	Industrial questionnaire suggested relesases of 0.0006 to 0.44 percent of benzene produced; average of 0.22 percent	Low: (0.0006%) (4,780,000 kkg produced in 1978) = High: (0.44%) (4,780,000) = Average: (0.22%) (4,780,000) =	30 Low 21,000 High 11,000 Average

figures are for benzene production for all processes: the petroleum-based processes discussed in this section and the coal-based production treated in Section 2.2. From their data, a factor for generation of solid wastes from benzene production was derived.

$$\frac{\begin{pmatrix}\text{Solid Waste from}\\ \text{Benzene Production,}\\ 1972\end{pmatrix}}{\begin{pmatrix}\text{Benzene Produced,}\\ 1972\end{pmatrix}} = \begin{matrix}\text{Solid Waste}\\ \text{per kkg of}\\ \text{Benzene Produced}\end{matrix}$$

$$\frac{(12{,}508\text{ kkg})}{(4{,}170{,}492\text{ kkg})} = 0.003$$

JRB estimates that 1 percent of the solid waste is benzene. Recovery of this concentration of benzene would be uneconomical; therefore, its presence in solid waste is plausible. This estimate is also consistent with our understanding of the industry and with comments made by industrial officials contacted.

Benzene releases to solids as a result of benzene production from petroleum and coal tar are as follows:

$$\begin{pmatrix}\text{Benzene}\\ \text{Produced,}\\ 1978\end{pmatrix}\begin{pmatrix}\text{Solid Waste}\\ \text{Generation}\\ \text{Factor}\end{pmatrix}\begin{pmatrix}\text{Percent}\\ \text{Benzene in}\\ \text{Solid Waste}\end{pmatrix} = \begin{matrix}\text{Benzene}\\ \text{Released to}\\ \text{Solid Waste}\end{matrix}$$

Petroleum

$$(4{,}710{,}000\text{ kkg})(0.003)(0.01) = 141\text{ kkg}$$

Coal Tar

$$(252{,}000\text{ kkg})(0.003)(0.01) = 8\text{ kkg}$$

JRB estimated that the solid wastes generated from benzene production would be handled in the same manner as those from refineries, which are sent to a land disposal site. For more information on refining waste disposal refer to Section 3.1.

2.1.8 Releases of Benzene Due to Transportation, Loading, and Storage Associated with Production of Petroleum

In addition to benzene releases from the four methods of producing benzene from petroleum, releases also occur during the flow of benzene from the producer to users. These releases may occur during three transport processes: transportation, loading, and storage. The environmental releases of benzene are almost all to air (99 percent), with the remainder going to water as a result of barge transportation of benzene.

2.1.8.1 Sources of Benzene Releases During Storage

Benzene is stored in one of the three types of floating-roof storage tanks: pan, pontoon, and double-deck. The pontoon and double-deck tanks were designed to alleviate two problems with the pan type:

- Extreme tilting of the pan may cause the roof to buckle or sink, resulting in a large loss of benzene vapor to the atmosphere.
- Contact between the benzene liquid and a directly heated roof by the sun may cause the benzene to boil, resulting in emission of benzene vapors to the atmosphere.

All tanks lose vapor at gauging hatches, sample hatches, and relief vents unless these points are designed and maintained for proper closure. Also, if the seal between the roof and vessel is improperly fitted, exposure of the liquid surface may result in emissions (PEDCo 1977).

Benzene releases due to storage are classified as standing and withdrawal losses. Storage standing loss is caused by the previously mentioned factors and increases with the length of storage time. Withdrawing benzene from the tank increases the amount lost, usually from the evaporation of benzene retained on the sides of the tank as the roof sinks (PEDCo 1977).

Release factors for storage standing and storage withdrawal losses are presented in Table 2.15.

By applying the first two factors listed in the table and the conversion factor of 3.33×10^{-3} kkg/gallon to the total 1978 benzene consumption of 5,389,000 kkg (Section 5.1), it was estimated that 100 kkg of benzene were lost due to standing storage, and 5.4 kkg were lost due to storage withdrawal. The sum of these was 105 kkg lost to air due to storage. In contrast, applying the SRI release factor for uncontrolled storage (for a maximum value) to total benzene consumption in 1978 and assuming that all benzene consumed had been stored, yielded a value of 4,900 kkg for benzene lost due to storage. In the absence of information that would permit choosing between these two disparate release estimates, the releases to air due to storage are assumed to be in the range of 105 to 4,900 kkg.

2.1.8.2 Sources of Benzene Releases During Loading

Benzene is transported by railroad tank cars, tank trucks, barges on inland waterways, and pipelines. Before benzene is transported, it is first collected and temporarily stored in a "rundown tank," where it is inspected for product quality. Then it is transferred to two sets of shipping tanks, one for railcar and truck loading and the other for barge loading. The rail and truck loading tank is also used to feed pipelines. Benzene losses from these tanks may be characterized as standing losses (caused by evaporation around perimeter roof seals) and withdrawal losses (caused by emptying the tank). Release factors for these processes are presented in Table 2.16 (Dunavent 1978).

Table 2.15 Benzene Release Factors and Calculations for Storage Releases

Source	Release Factors	Derivation
Based on PEDCo 1977	Storage: standing 8×10^{-8} kkg/gal of benzene consumed	$\frac{(30)(4.6 \times 10^{-3})}{(0.75)(2.3 \times 10^{6})}$ 30 = retention time in days (estimated) 4.6×10^{-3} = tank emission factor in kkg/tank/day 0.75 = percent of tank filled (estimated) 2.3×10^{6} = size of average storage tank (gal)
PEDCo 1977	Withdrawal 3.4×10^{-9} kkg/gal of benzene consumed	$\frac{(7.4 \times 10^{-6})}{(2.2 \times 10^{3})}$ 7.4×10^{-6} = withdrawal loss in lbs/gal 2.2×10^{3} = lbs/kkg
SRI 1978	Uncontrolled Storage 3.0×10^{-6} kkg/gal of benzene stored Internal Floating Roof coupled with vapor recovery system 0.3×10^{-6} kkg/gal	SRI included these estimates when calculating releases from certain refineries as presented in Figure 3.1.

Table 2.16 Benzene Release Factors and Calculations for Loading Operations

(Source: Based on Dunavent 1978)

Release Factor	Derivation
Rundown Tank Losses	Converted from estimated releases for a 40 x 10^6 gal capacity petroleum-derived benzene plant working at capacity.
Standing: 6.4×10^{-8} kkg/gal	$\frac{5{,}600 \text{ lbs emitted}}{2.2 \times 10^3 \text{ lbs/kkg}} \div 40 \times 10^6$ gal
Withdrawal: 5.8×10^{-8} kkg/gal	$\frac{5{,}100 \text{ lbs}}{2.2 \times 10^3 \text{ lbs/kkg}} \div 40 \times 10^6$ gal
Rail/Truck Loading Tank Losses	Converted from estimated releases for a 40 x 10^6 gal capacity petroleum-derived benzene plant working at capacity; 28 x 10^6 gal of this are handled through rail/truck loading tanks (14 x 10^6 gal of this later placed in pipeline); the remaining 12 x 10^6 gal are handled through barge loading tanks.
Standing: 1.7×10^{-7} kkg/gal loaded	$\frac{10{,}200 \text{ lbs}}{2.2 \times 10^3} \div 28 \times 10^6$ gal
Withdrawal: 3.6×10^{-8} kkg/gal loaded	$\frac{2{,}200}{2.2 \times 10^3} \div 28 \times 10^6$ gal
Barge Loading Tank Losses	
Standing: 4.6×10^{-7} kkg/gal loaded	$\frac{12{,}100}{2.2 \times 10^3} \div 12 \times 10^6$
Withdrawal: 3.0×10^{-8} kkg/gal loaded	$\frac{800}{2.2 \times 10^3} \div 12 \times 10^6$
Loading Losses	Assume: 10 x 10^6 gal loaded in rail tanker; 4 x 10^6 gal loaded in truck tankers; and 12 x 10^6 loaded in barges.
Railtanker: 1.3×10^{-6} kkg/gal loaded	$\frac{28{,}900}{2.2 \times 10^3} \div 10 \times 10^6$ gals
Truck: 1.3×10^{-6} kkg/gal loaded	$\frac{11{,}600}{2.2 \times 10^3} \div 4 \times 10^6$ gals
Barge: 1.1×10^{-6} kkg/gal loaded	$\frac{28{,}900}{2.2 \times 10^3} \div 12 \times 10^6$ gals

Loading losses are produced as liquid benzene is pumped into the carrier and vapors present (either from previous loads or currently generated) are displaced. Release factors for rail, tankers, trucks, and barges are also presented in Table 2.16 (Dunavent 1978).

Before applying these release factors, it was necessary to determine the quantity of benzene that was not captively used in production of benzene derivatives. First the capacity for noncaptive production was derived:

$$\begin{pmatrix}\text{Total Capacity,}\\ \text{1978}\end{pmatrix} - \begin{pmatrix}\text{Captive}\\ \text{Capacity}\end{pmatrix} \qquad \begin{matrix}\text{Noncaptive}\\ \text{Capacity}\end{matrix}$$

$$(2{,}125 \times 10^6 \text{ gal}) - (987 \times 10^6 \text{ gal}) = 1{,}138 \times 10^6 \text{ gal}$$

These figures are based on data from USITC, Arthur D. Little, Inc. (1977), and SRI (1977). For benzene producers listed as partial captive consumers, production was estimated to be 50 percent captive.

By applying this information to the total benzene production by refineries (including extraction of light oil), the noncaptively consumed benzene for 1978 was calculated.

$$\frac{\begin{pmatrix}\text{Captive}\\ \text{Capacity}\end{pmatrix}}{\begin{pmatrix}\text{Total}\\ \text{Capacity}\end{pmatrix}} (\text{Refinery Production, 1978}) = \begin{matrix}\text{Benzene}\\ \text{Noncaptively}\\ \text{Consumed, 1978}\end{matrix}$$

$$\frac{(1{,}138 \times 10^6 \text{ gal})}{(2{,}125 \times 10^6 \text{ gal})} (4{,}780 \times 10^3 \text{ kkg}) = 2{,}560 \times 10^3 \text{ kkg}$$

This value was used in combination with the release factors for loading operations in Table 2.16 to calculate the total benzene release due to loading operations. The following assumptions were necessary for these calculations:

- All the noncaptive benzene passes through rundown tanks.
- Fifty percent of the noncaptive benzene is loaded into railroad tanks or trucks; the remaining 50 percent is loaded in barges.

These calculations yielded the following release estimates:

From rundown tanks:	
Standing:	49 kkg
Withdrawal:	45 kkg
From railroad/truck loading tanks:	
Standing:	64 kkg
Withdrawal:	14 kkg
From barge loading tanks:	
Standing:	176 kkg
Withdrawal:	12 kkg
From loading losses to:	
Railcars/trucks:	500 kkg
Barges:	423 kkg

Total Benzene Releases Due to Loading Operations:

1,300 kkg

No independent criteria were available for determining uncertainty ranges of these estimates.

2.1.8.3 Releases During Transit

Release factors for releases during transit are summarized in Table 2.17. The PEDCo factor assumes equal distribution between rail/truck and marine transit, and does not include releases due to loading and unloading. Applying this factor to the amount of benzene not captively used in 1978 (2,560 x 10^3 gallons) yields an estimate of 270 kkg of benzene lost due to transit.

The SRI factors were derived for specific modes of conveyance. It is not known whether these factors include releases due to loading and unloading operations. In applying these factors we assumed that 50 percent of transport was by rail or truck and 50 percent by barge.

Releases from noncaptive benzene (2,560 x 10^3 kkg) calculated from these factors were as follows:

From transit by rail and truck:	690 kkg
From transit by barge:	290 kkg
	980 kkg

No independent criteria were available with which to judge the uncertainty ranges of these estimates.

Table 2.17 Benzene Releases and Calculations for Transportation

Source	Factors (kkg/gal)	Remarks
Based on PEDCo 1977	Transit 3.6 x 10^{-7}	Transport time 1 week Conveyance: 50 percent truck/rail tankers, and 50 percent barge Losses from loading/unloading are excluded from factor
SRI 1978	Uncontrolled Conditions Inland Barge 0.76 x 10^{-6} Tank Truck 1.8 x 10^{-6} Rail Tanker 1.8 x 10^{-6}	Not known whether factors include losses from loading/unloading

2.1.8.4 Total Releases Due to Transportation, Loading, and Storage

The sum of estimated emissions for transport, loading, and storage operations for petroleum-derived benzene was:

$$\begin{pmatrix}\text{Storage}\\ \text{Releases}\end{pmatrix} + \begin{pmatrix}\text{Loading}\\ \text{Releases}\end{pmatrix} + \begin{pmatrix}\text{Transport}\\ \text{Releases}\end{pmatrix} = \text{Total}$$

$$(105 - 4{,}900\ \text{kkg}) + (1{,}300\ \text{kkg}) + (980\ \text{kkg}) = 2{,}400 - 7{,}200\ \text{kkg}$$

Since the release factors were predominantly concerned with evaporation losses, the benzene releases of 2,400 to 7,200 kkg is considered a loss to air. This range of releases is intended to be neither a statistical range nor a set of error limits. It was not possible to estimate the uncertainties of the release factors used; therefore, the uncertainties of the release estimates could not be determined.

2.2 BENZENE PRODUCTION FROM COAL

2.2.1 Summary

Figure 2.2 shows the production and location of producers of benzene from coal. Company names and locations were compiled from information reported by Versar (1979) and Neufeld et al. (1978). Estimated production for the years 1975 to 1979 was calculated using the following formula:

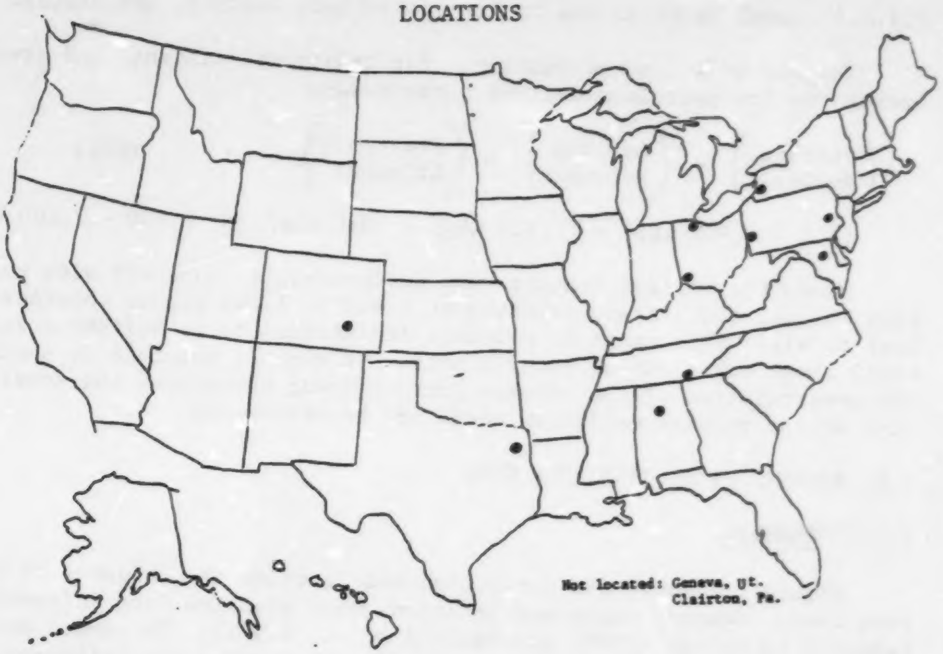
$$\frac{\begin{pmatrix}\text{Total U.S. Production,}\\ \text{Coal-Derived Benzene}\end{pmatrix}\begin{pmatrix}\text{Plant}\\ \text{Capacity}\end{pmatrix}}{(\text{Total U.S. Capacity})} = \begin{matrix}\text{Plant Production}\\ \text{of Benzene}\\ \text{from Coal}\end{matrix}$$

In calculating the production of benzene from coal for the years 1975 through 1979, the production figures used were obtained from USITC, and capacity information was taken from Versar (1979), SRI (1977), and Neufeld et al. (1978). Production for 1979 was based on USITC data for January through July, and extrapolated to cover the whole year. Plant capacities for 1975 were assumed to be the same as those for 1977, reported by SRI (1977) and Neufeld et al. (1978).

2.2.2 The Process

Benzene is produced as a byproduct of the carbonization of coal to coke. Coal is heated in an oven in the absence of air driving off the volatile gases. These hot gases are collected overhead and shocked-cooled with a flushing liquor, which results in the removal of a large portion of the tars and inorganic salts. The gases are further processed to remove additional tars and ammonia. The gas is cooled once more with water, then scrubbed with a high-boiling absorbent petroleum oil in a tall column. The wash oil removes the light oil containing benzene, toluene, xylene, etc., from the gas, and the mixture of wash and light oils is separated by steam distillation. The crude light oil consists of 55 to 70 percent benzene by volume (Arthur D. Little, Inc. 1977). The yield of light oil from coke ovens producing blast furnace coke is 3 to 4 gallons per ton of coal carbonized (PEDCo 1977).

LOCATIONS



Not located: Geneva, Ut.
Clairton, Pa.

PRODUCTION OF BENZENE FROM COAL

Coal-derived Benzene Producers[1]		Estimated Production (kkg)[2]					Plant Capacities Used in Estimations: 10^6 gal[3]		
Company	Location	1979	1978	1977	1976	1975	1978-79	1977	1975-76
Armco Steel Corp.	Middletown, OH	6,500	5,700	7,300	6,400	6,900	3	3	3
Bethlehem Steel Corp.	Bethlehem, PA	8,700	7,700	9,800	8,600	9,200	4	4	4
	Lackawanna, NY	0	0	0	17,000	18,000	0	0	8
	Sparrows Point, MD	33,000	29,000	37,000	32,000	35,000	15	15	15
Mead Corporation	Chattanooga, TN	0	0	0	0	0	0	0	0
	Woodward, AL	4,400	3,800	4,900	0	0	2	2	0
C.F. & I. Steel Corp.	Pueblo, CO	6,500	5,700	7,300	6,400	6,900	3	3	3
Interlake, Inc.	Toledo, OH	2,200	1,900	2,400	2,100	2,300	1	1	1
Jones & Laughlin Steel Corp. (LTV Corp)	Aliquippa, PA	22,000	19,000	24,000	21,000	23,000	10	10	10
Northwest Industries, Inc. (Lone Star Steel Corp)	Lone Star, TX	2,200	1,900	2,400	2,100	2,300	1	1	1
U. S. Steel Corp.	Clairton, PA	109,000	96,000	110,000	96,000	104,000	50	45	45
	Geneva, UT	8,705	7,700	9,800	8,600	9,200	4	4	4
Actual Total Production by U. S. Coke Oven Operators (kkg) (USITC)		202,397	178,062	215,021	201,169	216,617	93	88	94

1. Sources: Versar, 1979; Neufeld *et al.*, 1978.

2. Estimates for individual plants based on capacity estimates. See section 2.2.2.

3. Sources: Versar, 1979; SRI, 1977; Neufeld *et al*;,1978.

Figure 2.2 Coal-Derived Benzene Producers

Another source of light oil is coal tar. Coal tar can be distilled to yield a light oil fraction which is usually combined with the light oil from coal gas before it is refined to produce benzene (PEDCo 1977). Light oil produced is either refined on-site or is sold. Several petroleum producers refine this coal-derived light oil (SRI 1977; Arthur D. Little, Inc. 1977).

The light oil is refined by various processes that result in separation into benzene, toluene, xylene, and residue fractions. Benzene recovered from coke oven gas typically amounts to 1.85 gallons per ton of coal carbonized (PEDCo 1977).

A schematic diagram summarizing benzene production from coal is presented in Appendix B.

2.2.2.1 Amount Produced

In 1978, 178,000 kkg of coal-derived benzene were produced, according to USITC. This represented 4 percent of total benzene production.

2.2.2.2 Releases During Coal-Derived Benzene Production

Possible sources of release during production of benzene from coal are presented in Table 2.18. No release factors or data from which release factors could be calculated were found in the literature for the production of benzene from coal. Therefore, no benzene releases attributed to benzene production from coal coking were calculated. Release factors for the coal coking process in general were obtained from the literature and are presented in Section 3.3 (Indirect Production of Benzene). No release factors for transportation, loading, and storage of coal-derived benzene were obtained from the literature, nor could they be derived; consequently, no releases were calculated.

Table 2.18 Possible Sources of Benzene Releases from Coal Coking

Process Source	Estimated Type of Release
Shock cooling of flushing liquor (removing tars and inorganic salts)	Shock liquor may contain benzene tars; inorganic salts may be contaminated with benzene
Tar and ammonia removal	Tar with ammonia may be contaminated with benzene
Second water cooling	Water may contain benzene
Scrubbing process (washing with higher boiling oils)	Petroleum oil contains benzene
Wash oil/light oil separation over steam distillation	Wash oil contains residual benzene; steam condensates contain benzene
Light oil separation	Light oil contains residual benzene

2.3 SUMMARY

The total amount of benzene produced in the United States in 1978, according to USITC, was 4,960,000 kkg, of which 4,710,000 kkg were petroleum-derived and 252,000 kkg were coal-derived. For further breakdown by process refer to Table 2.19.

The total estimated releases from petroleum-derived benzene are between 6,424 and 11,219 kkg. Refer to Table 2.20 for a breakdown of these releases.

The amounts of releases that can be specifically attributed to coal-derived benzene are not known. Releases from this source are included in releases from coke ovens that are presented in Section 3.2.

Table 2.19 Total Benzene Produced in the United States During 1978

Feedstock Derivation	Processes	Quantity of Benzene Produced per Process (kkg)
Petroleum	Catalytic reformation	2,360,000
	Dealkylation	1,300,000
	Disproportionation-Transalkylation	121,000
	Pyrolysis Gasoline	925,000
	Total, Petroleum	4,710,000
Coal	Coke oven	178,000
	Extraction of purchased light oil and unnamed methods	74,000
	Total, Coal	252,000
	Total, Both Sources	4,960,000

Table 2.20 Total Benzene Releases Due to Petroleum-Derived Benzene Production in 1978

Source of Release	Benzene Releases (kkg)
Production Methods	
Catalytic reformation	2,500
Dealkylation	1,300
Disporportionation-Transalkylation	60
Pyrolysis gasoline	180
Total, Production	4,000
Transport	980
Loading	1,300
Storage	105 - 4,900
Total, Other Processes	2,400 - 7,200
Total, Petroleum-Derived Benzene Losses	6,400 - 11,200

3.0 INDIRECT PRODUCTION OF BENZENE

3.1 INDIRECT PRODUCTION OF BENZENE FROM REFINING OPERATIONS

It is estimated that crude oil contains an average of 0.2 percent benzene (Walker 1976). Therefore, petroleum refining operations are expected to be a source of benzene releases. The literature revealed several release factors for benzene to air and to water. These are presented in Table 3.1.

The Mara and Lee (1978) factors were based on average refinery hydrocarbon releases, a small percentage of which are benzene. Mara and Lee estimated that hydrocarbon releases from refineries with catalytic reforming capacity would be double those of other refineries. The doubling is attributed to storage losses for gasoline, which is apparently produced from catalytic reformate exclusively. Other sources of releases are leaks and stacks. Using a list of petroleum refineries and their capacities, Mara and Lee applied these factors to determine total benzene releases to air. Releases due to storage and loading of pure benzene were estimated and combined for those refineries producing non-captively consumed benzene. Controlled releases were assumed only for those refineries for which information on release control technology was known. Full-capacity production was assumed. These releases for each state are presented in Figure 3.1. Total U.S. benzene releases to air from petroleum refineries operating at 1977 capacity were estimated by this method to be 20,000 kkg.

The PEDCo release factors were considerably lower than those of Mara and Lee. The largest PEDCo factor, that for uncontrolled refineries, was half as large as the smallest Mara and Lee factor. The Mara and Lee factors were used to present a maximum value.

One factor for releases to water from petroleum refining was calculated from data presented by Versar (1977). In Effluent Guidelines Division of EPA, sampling data for six refineries collected by Versar showed that one refinery had a benzene concentration of 6 μg/ℓ in its effluent, while no benzene was detected in effluents of the other five. Benzene release allocated to water from refineries was calculated by developing a formula from the following factors:

- An average benzene concentration of 1 μg/ℓ
- The average quantity of water used per barrel of refined crude
- The number of refineries that directly discharge their effluents
- The number of barrels refined in 1978
- Metric conversion units.

These factors were used by JRB to calculate the water release factor in Table 3.1. The reliability of this factor is low due to the small amount

Table 3.1 Benzene Release Factors for Petroleum Refineries

Reference	Release Factor	Derivation of Release Factors
		Releases to Air
Mara and Lee (1978)	*$\frac{\text{4.6 lbs Benzene}}{\text{1,000 bbl crude refined}}$	Calculated from $\frac{\text{920 lbs}}{\text{1,000 bbl}}$ (0.5%) where 920 lbs = estimated hydrocarbon releases per 1,000 bbl and (0.5%) = estimated % of hydrocarbons attributed to benzene. Applies to refineries without catalytic reformation benzene production
	*$\frac{\text{9.2 lbs Benzene}}{\text{1,000 bbl crude refined}}$	Calculated from $\frac{\text{920 lbs}}{\text{1,000 bbl}}$ (1.0%) where 1.0% = estimated % of hydrocarbons attributed to benzene. Applies to refineries with catalytic reformation benzene production
PEDCo (1977)	0.415 lbs/1,000 bbl	For controlled refineries
	2.27 lbs/1,000 bbl	For uncontrolled refineries
	0.759 lbs/1,000 bbl	Weighted industry average
		Releases to Water
Based on Versar (1977)	1.64×10^{-10} kkg/bbl	(1 μg/l)(43.36 gals water used per bbl)(3.785 l/gal) x (10^{-12} kkg/μg) From Effluent Guidelines Division data: benzene was detected in 1 of 6 refineries at 6 μg/l, therefore average concentration is 1 μg/l.

*Factor used in Figure 3.1

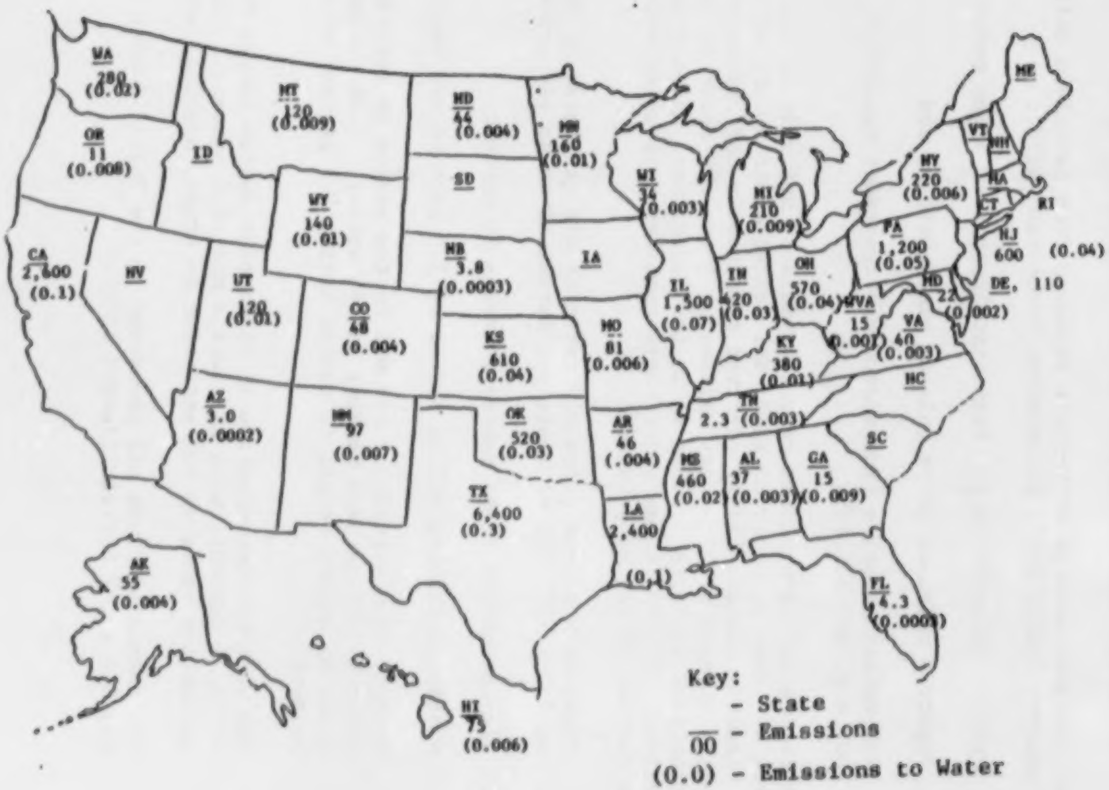

WA
280
(0.02)
OR
11
(0.008)
CA
2,600
(0.1)
NV
ID
MT
120
(0.009)
WY
140
(0.01)
UT
120
(0.01)
AZ
3.0
(0.0002)
CO
48
(0.004)
NM
97
(0.007)
ND
44
(0.004)
SD
NB
3.8
(0.0003)
KS
610
(0.04)
OK
520
(0.03)
TX
6,400
(0.3)
MN
160
(0.01)
IA
MO
81
(0.006)
AR
46
(.004)
LA
2,400
(0.1)
WI
34
(0.003)
IL
1,500
(0.07)
MI
210
(0.009)
IN
420
(0.03)
OH
570
(0.04)
KY
380
(0.01)
TN
2.3 (0.003)
MS
460
(0.02)
AL
37
(0.003)
GA
15
(0.009)
FL
4.3
(0.0001)
SC
NC
VA
40
(0.003)
WVA
15
(0.001)
MD
22
(0.002)
DE, 110
PA
1,200
(0.05)
NY
220
(0.006)
NJ
600 (0.04)
CT
RI
MA
VT
NH
ME
AK
55
(0.004)
HI
73
(0.006)
Key:
- State
00 - Emissions
(0.0) - Emissions to Water

Figure 3.1 Benzene: Refinery Emissions by State (kkg)

Sources: Mara and Lee, 1978; Versar, 1977 of data upon which it was based. It was the only emission factor available for benzene releases to water from petroleum refining; consequently, it was applied to the petroleum refining capacities listed by Mara and Lee (1978) in order to provide an order of magnitude estimate. JRB assumed full-capacity production and direct discharge of effluent for all refineries. The results of our calculations appear on the map in Figure 3.1 as state totals. Total benzene releases to water generated at U.S. refineries were calculated to be 1 kkg during 1978.

The possible sources of benzene releases from petroleum refineries are as follows (PEDCo 1977; Hydrocarbon Processing 1978):

- Process releases (e.g., from distillation of light ends);
- Fugitive releases (from valves, pumps, etc.); and
- Nonprocess releases from wastewater treatment facilities, heaters, and boilers.

Petroleum refinery wastes vary considerably not only in the amounts produced, but also in water content, oil content, and amount of inert matter present. Jacobs (1979) reported the amounts and characteristics of 17 waste streams at a typical refinery. These are shown in Table 3.2. From these data and from inferences in the literature, release factors were derived. The following points were considered in calculating the benzene content of refinery wastes:

1. Total wastes from petroleum refining are generated at the rate of 7.7×10^{-4} kkg of waste per barrel of crude oil processed.
2. Oil content in these wastes averages 16 percent.
3. Wastes containing oil in excess of 3.5 percent are recycled.
4. Seventy-five percent of the oil in the wastes is recovered, and the other 25 percent remains in the wastes. (JRB estimation based on amount of oil in wastes having 3.5 percent or more benzene).
5. The benzene concentration in these oily wastes ranges from 0.1 to 1 percent, with an average near 0.5 percent. (JRB estimation based on concentration in crude, naphtha, etc.).
6. The amount of crude oil processed in the United States in 1978 was 5.0×10^9 barrels (Jacobs 1979).

The quantity of benzene in refinery waste is calculated as follows:

$$(\text{Crude Processed}) \begin{pmatrix}\text{Waste Generation}\\ \text{Factor}\end{pmatrix} \begin{pmatrix}\text{Fraction of Oil}\\ \text{in Wastes}\end{pmatrix} \times$$

$$(5.0 \times 10^{9} \text{ barrels}) \begin{pmatrix}7.7 \times 10^{-4} \text{ kkg/}\\ \text{barrel}\end{pmatrix} (0.16) \times$$

$$\begin{pmatrix}\text{Fraction of Oil}\\ \text{That Remains in}\\ \text{Wastes}\end{pmatrix} \begin{pmatrix}\text{Fraction of}\\ \text{Benzene in Oily}\\ \text{Wastes}\end{pmatrix} = \begin{matrix}\text{Benzene in}\\ \text{Wastes from}\\ \text{Petroleum Refining}\end{matrix}$$

$$(0.25) \qquad (0.005) = 770 \text{ kkg}$$

This quantity is subdivided by type of disposal methods as stated by Jacobs 1979 in Table 3.2.

Table 3.2 Petroleum Industry Disposal of Wastes Containing Benzene

Disposal Method[1]	Refining (%)[1]	Wastes (kkg)	Benzene Disposed (kkg)
Landfilling	51.1	5.88×10^{8}	393
Landspreading	8.4	0.97×10^{8}	65
Lagooning	39.7	4.57×10^{8}	306
Incineration	0.8	0.09×10^{8}	6

[1] Adapted from Jacobs (1979).

3.2 BENZENE RELEASES FROM COAL COKING OPERATIONS

The coke capacity of the 65 facilities producing coke in the United States was 88,000,000 kkg (Mara and Lee 1978). Ten of these coke facilities, with combined annual capacity of 25,600,000 kkg, produce benzene as a byproduct from coal-derived light oil (PEDCo 1977; Mara and Lee 1978). According to Arthur D. Little, Inc. (1977), 50 percent of the light oil was used by ten coke-producing facilities for extraction of benzene; the remaining 50 percent is sold to petroleum refineries for benzene extraction. We assumed that the ten facilities referred to by Little were the same facilities identified by PEDCo, and that these facilities processed all their light oil to extract benzene. The remaining 55 facilities, with an annual coke capacity of 62,700,000 kkg (Mara and Lee 1978), were assumed to produce the light oil sold to petroleum refiners.

The quantity of light oil produced was calculated by applying a factor of 3.5 gallons of light oil produced per kkg of coke produced (PEDCo 1977). The quantity of light oil produced by the ten coke facilities reported to extract benzene is presented below:

$$\left(\begin{array}{c}\text{Coke Produced by}\\ \text{10 Facilities that}\\ \text{Extract Benzene}\end{array}\right)\left(\begin{array}{c}\text{Light Oil}\\ \text{Produced per}\\ \text{kkg of Coke}\end{array}\right) = \begin{array}{c}\text{Light Oil}\\ \text{for Benzene}\\ \text{Extraction}\end{array}$$

$$(2.56 \times 10^7 \text{ kkg}) \qquad (3.5 \text{ gal/kkg}) = 8.96 \times 10^7 \text{ gal}$$

By applying the same formula, the remaining 55 facilities had production capacity for 219,000,000 gallons of light oil. This is in sharp contrast to the 100,000,000 gallons (the "other half" of light oil production) that Little claims was sold to petroleum refineries. Some of the difference may be light oil that was used captively in various processes (Arthur D. Little, Inc. 1977). No information was obtained that would indicate where the remainder of this 119,000,000 gallons went. If some of this unaccounted-for light oil was not produced, then the materials that could have gone into this product must have been used elsewhere or released to the environment. A more intensive search is required to evaluate this potentially extremely large source of benzene releases.

Possible sources of benzene releases from coke oven operators, as indicated by PEDCo (1977) are:

1. Uncontrolled charging (placing coal into the oven). Evaporation and coking of volatile components occurs when coal contacts the hot oven floor. This is perhaps the greatest potential release source for hydrocarbons (including benzene).

2. Topside releases of fugitive benzene from many sources, including leakage from weakened refractory materials, ascension-pipe-elbow covers, leveling apertures, badly fitted charging-hold covers, and collecting main pipe valves.

3. Coke pushing (discharge of hot coke from the oven). This can be a major release source unless the coal is completely carbonized.

4. Door leaks, on both the push and coke sides of the oven.

5. Waste-gas stacks, if coal or coke escapes through leaks into areas between the oven and the heating flue.

6. Quenching (flooding of pushed hot coke with a huge quantity of cooling water). Much steam is produced, and releases would depend upon how completely the coal was carbonized.

The literature revealed three factors for benzene releases to air from coke oven operators. These are presented in Table 3.3.

The amount of benzene released to the air during coking operations was estimated using these three factors. When Walker's factor was used, we assumed that coking production was at full capacity, requiring consumption of 88,000,000 kkg of coal (derived from Table C-1 in Mara and Lee 1978); and that the yield of coke from coal is 68.4 percent. The value of 88,000,000 kkg of coal was used in calculations with the other release factors.

Table 3.3 Benzene Release Factors and Calculations for Coal Coking Operations

Reference	Release Factor	Derivation of Releases
Walker (1976)	$9.80 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg coke produced}}$	
PEDCo (1977)	$7.8 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	$(3.5 \times 10^{-3} \left(\frac{\text{kkg hydrocarbon}}{\text{kkg coal coked}}\right)$ (0.0223 fraction of benzene in total hydrocarbons) where $0.0223 = \left(\frac{0.776\% \text{ benzene in coke over year}}{34.8\% \text{ hydrocarbons in coke over year}}\right)$
Mara and Lee (1978)	$3 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	Estimated by multiplying the hydrocarbon release factor (4.2 lbs/ton coal) by the fraction of benzene in the total hydrocarbon release (0.0132). Based on EPA Document AP-42. The hydrocarbon release factor used here is different from the one used above. The factor for benzene content used here is different from that used above.

With the Walker factor, benzene releases were estimated to be:

$$\begin{pmatrix}\text{Coal to}\\ \text{Coke}\end{pmatrix} \quad \begin{pmatrix}\text{Coke}\\ \text{Yield}\end{pmatrix} \begin{pmatrix}\text{Benzene per}\\ \text{kkg of Coke}\end{pmatrix} = \text{Benzene Released}$$

$$(8.8 \times 10^{7} \text{ kkg}) \quad (68.4\%) \quad (9.8 \times 10^{-4}) = 5.9 \times 10^{4} \text{ kkg}$$

With the PEDCo factor, benzene releases to air were calculated as 6,900 kkg; the corresponding value derived with the Mara and Lee factor was 3,000 kkg.

The Mara and Lee factor was also applied to capacities by state to derive a distribution map of benzene releases from coke ovens (Figure 3.2).

No release factors for benzene to water from coke ovens were reported by the literature. Therefore, no releases could be calculated.

The precision of release estimates based on the Walker release factor was estimated to be ± a factor of 6, based on evaluation of the assumptions entering into derivation of the factor. The uncertainty is probably due almost entirely to the release factor.

3.3 INDIRECT PRODUCTION OF BENZENE FROM VARIOUS SOURCES

There are eight known indirect sources or contributors of benzene to the environment. These are covered in the subsequent sections.

3.3.1 Contamination of Benzene Co-Products

The production of benzene normally coincides with co-production of toluene, xylene, and/or hexane. These co-products are contaminated with benzene. One estimate of the quantity of benzene in these co-products is presented in Table 3.4. Toluene has the highest contamination (0.04 percent) and is produced in large quantities. Therefore, toluene contamination represents a significant quantity of benzene.

3.3.2 Benzene Contamination of Petroleum-Derived Products

Benzene contamination of other petroleum-derived products is presented in Table 3.5.

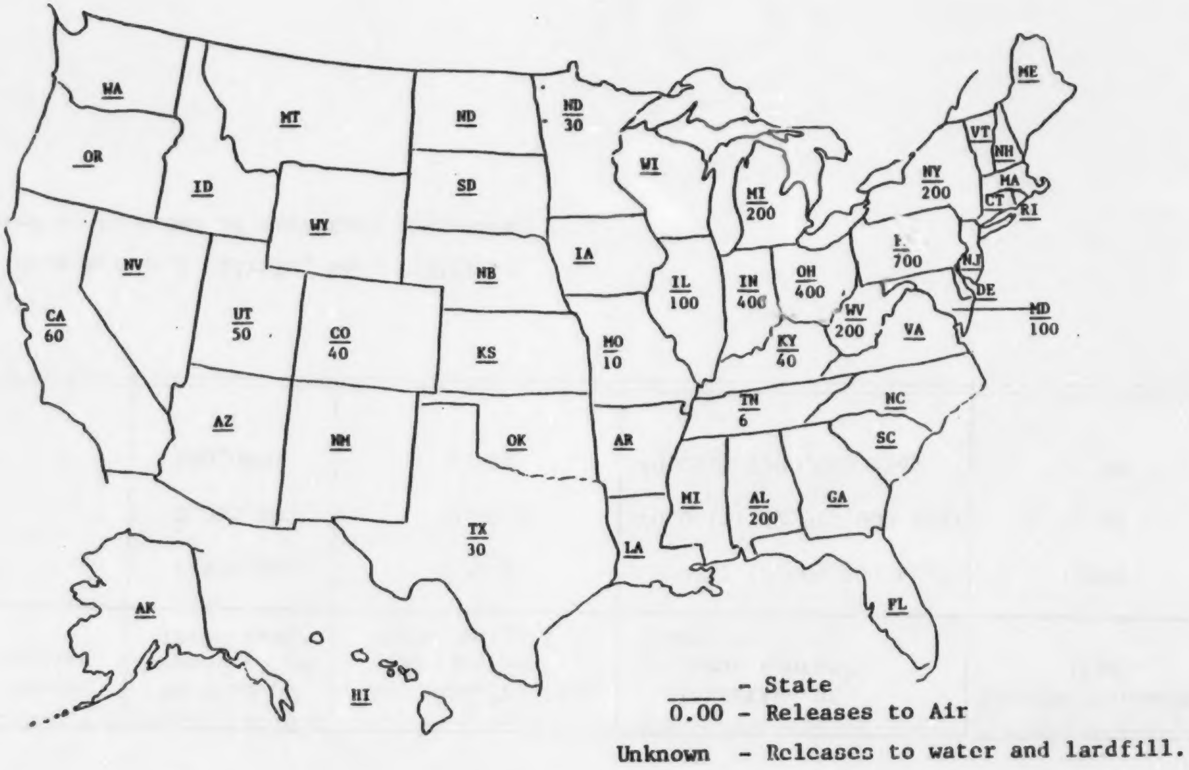

WA
OR
CA 60
NV
ID
MT
WY
UT 50
CO 40
AZ
NM
ND
SD
NB
KS
OK
TX 30
MN 30
IA
MO 10
AR
LA
WI
IL 100
MI 200
IN 400
OH 400
KY 40
TN 6
MI
AL 200
GA
FL
SC
NC
VA
WV 200
PA 700
NY 200
ME
VT
NH
MA
CT
RI
NJ
DE
MD 100
AK
HI
— State
0.00 - Releases to Air
Unknown - Releases to water and lardfill.

Figure 3.2 Benzene: Coke Oven Emissions by State (kkg)

Source: Mara and Lee 1978

Table 3.4 Co-Products of Benzene Production Contaminated with Benzene

Co-Products During Benzene Production	Co-Product Produced in 1978[1] (kkg)	Estimated Benzene Contamination[2] (% by weight)	Calculation of Benzene Contaminant	Benzene Contaminant[3] (kkg)
Toluene	2,404,000	0.04%	(0.04%) (2,404,000 kkg)	1,000
Xylene	2,915,000	0.001%	(0.001%) (2,915,000 kkg)	30
Hexane	200,000	0.02%	(0.02%) (200,000 kkg)	40

1. USITC 1978
2. Derived from Arthur D. Little, Inc. (1977).
3. Considered to be order of magnitude estimates.

Table 3.5 Estimated Benzene Content of Some Petroleum Products
(Source: Arthur D. Little, Inc. (1977)

Petroleum Products[1]	Estimated Benzene Content (% by Volume)
Solvent naphthas:	
Aromatic Petroleum	0-3
Stoddard	0-Trace
VM & P	0-3
Others	0-3
Coke-oven tar	0-0.3
Lubricating oils	0-Trace

1. Attempts to obtain production quantities were unsuccessful.

JRB was not able to obtain 1978 production figures for the petroleum products listed in Table 3.5. Due to the nature of the application of these products, JRB estimates that the benzene in these products would come in direct contact with consumers. The losses of benzene from these products would be to the air and municipal waste systems.

3.3.3 Benzene Precursors in Other Fractions

Contacts with industry indicated that individual companies and/or refineries differ with respect to the fraction (cut) of the crude oil that is selected for aromatic extraction. The cut is determined by the selected boiling range of components of the crude oil. The cut may cover many crude oil fractions which are further refined into specific components, or a specific cut may be taken for a particular fraction (such as aromatics). The usual cut in which aromatics are found is that for light naphtha, with boiling ranges of 80° to 220°C (Refinery Process Handbook 1978). Aromatics can also be obatined from a heavy naphtha cut (180° to 520°C) which has been heavily refined. It is plausible to assume that some of the benzene precursors (Table 3.6) are not extracted with the aromatic cut and end up in environmental conditions that facilitate the chemical formation of benzene. Therefore, those cuts of the crude oil that are above and below the naphthas cut could contain benzene precursors; under the proper conditions they would be a source of benzene releases to the environment.

3.3.4 Benzene in Gas Well Condensates

Benzene is a component of gas well condensates. One company, Atlas Processing (a subsidiary of Pennzoil), was reported to be producing small quantities of benzene from this source (SRI 1978). The company's benzene-producing wells are located in the East Texas gas fields.

Table 3.6 Benzene Precursors, Reaction and Crude Oil Fractions Containing Benzene Precursors

Benzene Precursors[1]	Reaction Causing Benzene Formation	Boiling Point (° C)	Crude Oil Fractions Containing the Benzene Precursor[4]
Benzene	All of the reactions below	80	Light naphtha 80° - 220° C
Hexane	Cyclodehydrogenation	69[2]	Gases below 80° C
Cyclohexane	Dehydrogenation	81[2]	Border between gases and light naphtha
Methylcyclohexane	Hydrogenation and	100[3]	Light naphtha 80° - 22° C
Dimethylcyclohexane	Dealkylation	120[1]	Light naphtha
Methylcyclopentane	Isomerization dehydrogenation	72[2]	Gases

1. SRI 1977
2. Morrison and Boyd 1966
3. Weast 1972
4. Weissermel 1978

JRB estimates that the geologic formations are probably similar throughout the eastern region of Texas and, therefore, other gas wells in the region also contain benzene. Attempts to obtain information on the fate of these condensates were unsuccessful. Further study is needed to determine the number of gas wells that have condensates containing benzene, the quantity of benzene contained in the condensates, and the types and quantities of releases to the environment.

3.3.5 Benzene Releases from Resource Mining and Processing Operations

The mining and processing of mineral, timber, and fiber resources produces some benzene releases to water. Table 3.7 shows estimates of benzene releases to water from these resources.

Table 3.7 Gross Annual Discharges of Benzene to Water in 1976 from Resource Obtaining and Processing

Process	Estimated Discharge of Benzene to Water (kkg/year)
Nonferrous metals manufacturing (Al, Cu)	2.85
Ore mining (Pb, Zn)	1.1
Wood processing	0.4
Coal mining	141.1
Textile industry (subcategories 40 and 60)	2.51

(Source: Versar 1977)

3.3.6 Benzene Releases from Oil Well Drilling

The drilling of oil wells produces environmental releases of benzene from drilling fluids, muds, and uncontrolled flow of crude oil above or below the surface. The quantity of benzene released is dependent on the percentage of benzene in the crude and the quantity of material containing crude oil (i.e., drilling muds and fluid). No information was obtained on the quantity of benzene released from this source of environmental release. JRB estimates that oil drilling sites are a potentially significant source of benzene releases.

3.3.7 Benzene Releases Due to Oil Spills

The environmental release of benzene from oil spills is dependent upon the quantity of benzene in the crude oil, the size of spill, the frequency of spills, and the location of the spill (surface or subsurface).

Walker (1976) estimated benzene releases to the oceans due to oil spills of all types using the following assumptions:

- Oil discharged to the oceans totaled 11.5 x 10^9 lb/year. This included both natural and man-caused events.

- Crude oil contains an average benzene concentration of 0.2 percent by weight (the range is reportedly 0.001 - 0.4 percent).

Total benzene releases to oceans were thus:

$$\text{(Oil Discharged)} \quad \begin{pmatrix}\text{Conversion}\\ \text{Factor}\end{pmatrix} \quad \begin{pmatrix}\text{Fraction}\\ \text{Benzene}\end{pmatrix} = \begin{matrix}\text{Benzene to Oceans}\\ \text{from Oil Spills}\end{matrix}$$

$$(11.5 \times 10^9 \text{ lbs}) \quad (4.54 \times 10^{-4} \text{ kkg/lb}) \quad (0.002) = 10.5 \times 10^3 \text{ kkg}$$

The uncertainty of the estimate is very large. The basis for the annual oil discharge value was not available, but the range of benzene concentration for oils introduces an uncertainty factor of 400 itself.

Versar (1977) estimated the gross annual discharge of benzene to U.S. waters from U.S. Coast Guard information on crude oil spills in 1976. This estimate was based on the following:

- The amount of crude oil lost to U.S. waters through spills in 1976 was 5 million gallons.

- Crude oil contains an average of 0.2 percent benzene by weight (range: 0.001 to 0.4 percent).

Benzene releases were estimated to be:

$$\text{(Oil Spilled)} \begin{pmatrix}\text{Fraction}\\ \text{Benzene}\\ \text{in Oil}\end{pmatrix} \quad \text{(Conversion Factors)} \quad = \begin{matrix}\text{Benzene to}\\ \text{U.S. Waters}\\ \text{from Oil Spills}\end{matrix}$$

$$(5 \times 10^6 \text{ gal}) \quad (0.002) \quad (7.21 \text{ lb/gal})(4.54 \times 10^{-4} \text{ kkg/lb}) = 30 \text{ kkg}$$

The uncertainty of this estimate is at least ± a factor of 400 (the range of benzene contents in crude oil).

3.3.8 Benzene Synthesized from Aliphatic Hydrocarbons

It is possible to synthesize benzene from straight-chain unsaturated hydrocarbons. Benzene can be synthesized from acetylene but is not done commercially because it is not economical. However, it is plausible to suggest that simple aliphatics, placed in the proper environmental conditions, would produce benzene. For example, it is possible that when the straight-chain unsaturated hydrocarbons in the earth's atmosphere are bombarded with ultraviolet rays, under certain conditions benzene could be created.

4.0 IMPORTS OF BENZENE

4.1 AMOUNT IMPORTED

Table 4.1 summarizes the amounts of benzene imported during the past five years.

Table 4.1 Benzene Imports, 1975-1979

Year	Imports (kkg)
1975	234,000
1976	175,000
1977	204,000
1978	225,000
1979	232,000[1]

(Source: Bureau of the Census, Department of Commerce)

[1] Based on extrapolation of January through October data for 1979.

4.2 RELEASES DUE TO IMPORTS

Releases in this category were interpreted as those due to unloading plus transport to the point of consumption. PEDCo (1977) estimated the following release factors for these processes: 2.0×10^{-4} kkg/kkg unloaded (uncontrolled), and 1×10^{-4} kkg/kkg transported per week.

In applying these release factors to 1978 imports, it was assumed that releases due to loading were 95 percent controlled at dockside, and that the average transit time for imported benzene was 1 week. Releases were then calculated as follows:

$$\left(\begin{matrix}\text{Imported}\\ \text{Benzene}\end{matrix}\right)\left[\left(\begin{matrix}\text{Loading}\\ \text{Release}\\ \text{Factor}\end{matrix}\right)\left(\begin{matrix}\text{Percent}\\ \text{not}\\ \text{Controlled}\end{matrix}\right) + \left(\begin{matrix}\text{Transport}\\ \text{Release}\\ \text{Factor}\end{matrix}\right)\left(\begin{matrix}\text{Time in}\\ \text{Transit}\end{matrix}\right)\right] =$$

Benzene release due to imports

$$(2.25 \times 10^{5} \text{ kkg}) \left[(2.0 \times 10^{-4})(0.05) + (1 \times 10^{-4}/\text{wk})(1 \text{ wk})\right] =$$

25 kkg

We estimate the uncertainty of this release to be ± a factor of 10, based on the difficulty of estimating release factors for processes of this type.

Of the total releases due to imports, 50 percent were judged to go to air and 50 percent to water. This estimate was based on the following considerations: most releases not attributable to accidental spillage would be to air because of benzene's volatility. In contrast, most accidental releases would ultimately be to water because transfer operations are at dockside and water would be used to hose down the area. This estimated distribution of releases gives 13 kkg of benzene released to air due to importation, and 13 kkg released to water.

There would be no releases of benzene to landfills or due to disposal of solid residues during importation.

5.0 CONSUMPTIVE USES AND EXPORTS OF BENZENE

The utilization of benzene can be broadly divided into consumptive and nonconsumptive uses. This chapter reports on releases due to consumptive uses: processes in which benzene is chemically converted to another compound. Nonconsumptive uses, in which benzene is used as an end product rather than as an intermediate, are discussed in Section 6.0. For the purposes of a materials balance, exports are considered consumptive uses because the chemical is permanently removed from the U.S. "inventory" by this process. Therefore, exports are also discussed in this chapter.

5.1 CONSUMPTIVE USES: TOTALS

Consumptive use of benzene in 1978 was estimated at 5,230,000 kkg. This total was derived in Table 5.1. The main use of benzene was as a chemical intermediate in the synthesis of other organics.

5.2 CATEGORIES OF USE

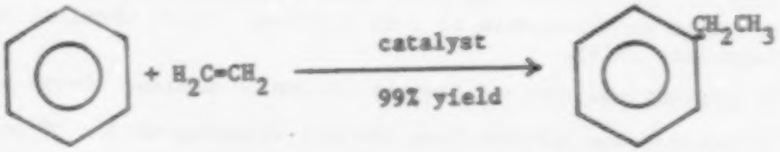
The major compounds derived from benzene in 1978 are listed in Table 5.1. In addition, minor uses are included in the environmental flow diagram for benzene, Appendix A. Ethylbenzene synthesis was by far the largest consumer of benzene, as it has been historically (see Table 5.2 for data on the years 1975-1979). The data in these two tables were based on USITC reports. Their uncertainties are not known, but are estimated to be small (less than ±20%).

5.3 RELEASES BY CATEGORY OF USE

5.3.1 Consumption of Benzene by Ethylbenzene Synthesis

5.3.1.1 Processes, Producers, and Locations

Approximately 90 to 95 percent of ethylbenzene is synthesized by alkylation of benzene with ethylene (Versar 1979; Weissermel and Arpe 1978; A.D. Little 1977):



Ethylbenzene
b.p. 136°C

The process is carried out in either liquid or vapor phase, with an excess of benzene to minimize diethylbenzene products. It is not known whether the liquid or vapor phase process predominates. The isolation of ethylbenzene as a production byproduct for xylenes and cumene accounts for the rest of ethylbenzene production. Appendix B-9 shows a process flow diagram for ethylbenzene synthesis.

TABLE 5.1 Consumptive Uses of Benzene, 1978

Use	Production[1] (kkg)	Benzene Required[2] (kkg)
Ethylbenzene	3,803,000	2,810,000
Cumene	1,533,000	1,030,000
Cyclohexane	1,057,000[4]	836,000
Nitrobenzene[3]	261,000	170,000
Chlorobenzenes (mono- plus di-)	172,000	134,000
Alkylbenzenes (linear plus branched)	330,000[5]	132,000
Maleic anhydride	155,000[6]	111,000
Biphenyl	29,000[7]	7,000
Total		5,230,000

1. USITC figures except as noted.
2. Conversion factors from Neufeld et al. 1978.
3. Includes nitrobenzene destined for aniline synthesis (96 percent) plus nonaniline usage (4 percent).
4. 85 percent was derived from hydrogenation of benzene (Blackford 1977).
5. Derived from 1978 USITC production figure for linear alkylbenzenes (239,000 kkg) using the 1978 ratio for capacities of linear to branched alkylbenzenes of 2.63 (Bradley 1979; Chemical Marketing Reporter 1979).
6. 84 percent was derived from oxidation of benzene (Gerry et al. 1979).
7. 30 percent was derived from thermal dehydrogenation of benzene.

TABLE 5.2 Consumptive Uses of Benzene, 1975-1979

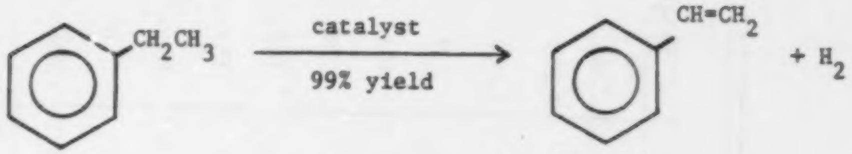
(Source: Neufeld et al. 1978)

Use	Benzene Consumed (1000 kkg)									
	1975		1976		1977		1978		1979[1]	
	1000 kkg	%	1000 kkg	%	1000 kkg	%	1000 kkg	%	1000 kkg	%
Ethylbenzene	1,760	48	2,380	51	2,580	53	2,810	54	2,910	52
Cumene	619	17	840	18	816	17	1,030	20	1,240	22
Cyclohexane	596	16	752	16	771	16	836	16	839	15
Nitrobenzene	228	6	169	4	228	5	170	3	187[2]	3
Maleic anhydride	115	3	137	3	120	2	111	2	172	3
Chlorobenzenes	140	4	151	3	151	3	134	3	145	3
Detergent alkylates	122	3	131	3	131	3	132	3	157	3
Biphenyl	9	0.2	9	0.2	9	0.2	7	0.1	n.a.	--
Benzenesulfonic acid	44	1	54	1	54	1	0	0	0	0
Total	3,634	98.9	4,627	99.9	4,857	100.9	5,230	101.1	5,650	101

1. Partial data from USITC were used to estimate these values

2. Estimated by the Operation: 1979 benzene consumption = $\frac{\text{(1979 aniline production)}}{\text{(1978 aniline production)}}$ X (1978 benzene consumption).

Almost all ethylbenzene is used for the subsequent production of styrene monomer (Versar 1979).



Styrene

This process is often integrated with ethylbenzene synthesis in a petrochemical complex, and benzene releases due to ethylbenzene synthesis are inseparable from those due to styrene synthesis (Hobbs and Key 1978).

Figure 5.1 lists ethylbenzene producers, estimated 1978 production by plant, and plant locations. At least 75 percent of ethylbenzene production is located along the Gulf Coast (Channelview, TX, and Welcome, LA, could not be located on the maps consulted). The plant capacity data were from SRI (1977). It was not possible to assess independently the reliability of these data. However, it was thought that the uncertainty of the total capacity was probably ±20%, since the values are obtainable from trade literature and are potentially verifiable by industry.

5.3.1.2 Amount of Benzene Consumed

In 1978, 2,810,000 kkg of benzene were used for the synthesis of ethylbenzene (Table 5.1). This value was obtained by the operation:

(kkg of Benzene Used) = (kkg of Ethylbenzene Produced)(Conversion Factor).

The conversion factor used was 0.74. This factor is equal to the ratio of the molecular weight of benzene to that of ethylbenzene, divided by the percentage theoretical yield. The latter was estimated to be 99 percent by Hatch and Matar (1978).

$$\frac{(\text{MW Benzene})}{(\text{MW Ethylbenzene})} \div \left(\frac{\text{Percent}}{\text{Yield}}\right) = \text{Conversion Factor}$$

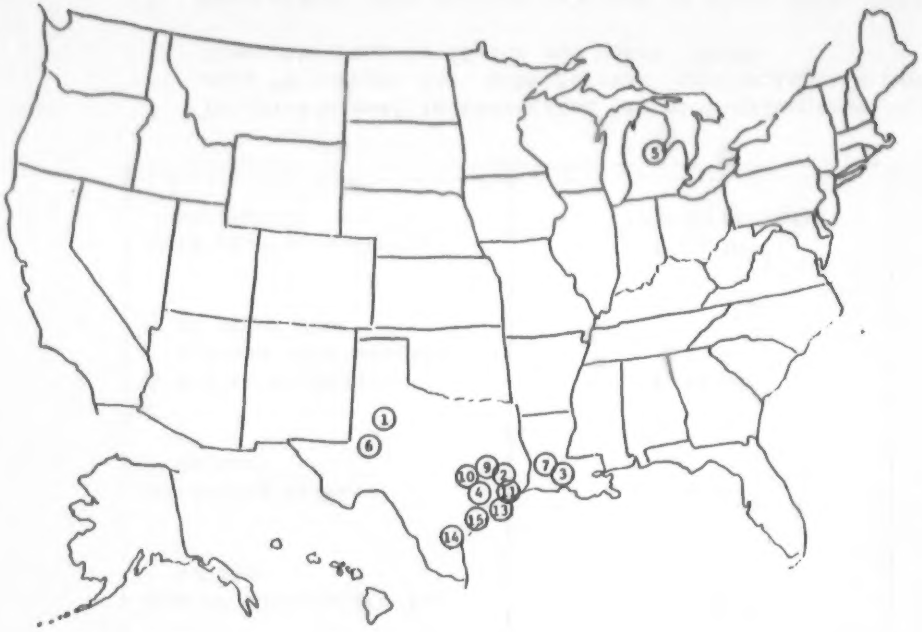
$$\frac{(78)}{(106)} \div (99\%) = 0.74$$

The uncertainty in the estimate of the amount of benzene consumed during ethylbenzene synthesis was ±20%.

5.3.1.3 Benzene Releases Due to Ethylbenzene and Styrene Synthesis

5.3.1.3.1 Generated Releases to Air

Previous studies have proposed release factors for benzene released to the air because of consumption processes. Table 5.3 summarizes the release factors used and the benzene releases calculated from them.



Map No.	Company	Plant Location	Ethylbenzene Production (kkg)
1.	American Petrofina	Big Spring, TX	Standby
2.	ARCO/Polymers, Inc.	Port Arthur, TX	101,000
3.	Cos-Mar, Inc.	Carville, LA	613,000
4.	Charter	Houston, TX	14,000
5.	Dow Chemical	Midland, MI	705,000
6.	El Paso Natural Gas	Odessa, TX	111,000
7.	American Hoechst	Baton Rouge, LA	467,000
8.	Gulf Oil Chemical	Welcome, LA	278,000
9.	ARCO/Polymers	Houston, TX	55,000
10.	Monsanto	Alvin, TX	24,000
11.	Monsanto	Texas City, TX	661,000
12.	Oxirane Chemical	Channelview, TX	466,000
13.	Standard Oil (Indiana)	Texas City, TX	254,000
14.	Sun Oil	Corpus Christi, TX	54,000
15.	Union Carbide	Seadrift, TX	Standby
			3,803,000

Source: Mara et al. 1979. Total ethylbenzene production (USITC 1979) was allocated to individual plants in proportion to their 1978 capacities.

Figure 5.1 Production of Ethylbenzene

Table 5.3 Summary of Estimated Benzene Releases to Air Due to Ethylbenzene and Styrene Synthesis

Source of Estimate	Release Factor[1] (kkg per kkg of benzene used)	Releases to Air, 1978 (kkg)	Reference
Sum of unaccounted-for benzene	1×10^{-2}	28,000	Howard and Durkin 1974
Estimated release factor[2]	5×10^{-3}	14,000	Patterson et al. 1976
Industry estimate, release rate measure at major vent	1.8×10^{-3}	5,100	PEDCo 1977
Site visits, industry estimates	1.4×10^{-3} (uncontrolled)	3,900	Hobbs and Key 1978

1. The yields used in converting kkg of ethylbenzene or styrene produced to kkg of benzene used were 99 percent for ethylbenzene synthesis from benzene and 90 percent for styrene synthesis from ethylbenzene (Hatch and Matar 1978).

2. Generalized from factors reported in AP-42 (EPA 1977).

The PEDCo release factor is equal to the following:

$$\begin{pmatrix}\text{PEDCo Factor}\\ \text{kkg of Benzene}\\ \text{Released per}\\ \text{kkg of Styrene}\end{pmatrix} \div \begin{pmatrix}\text{kkg of Benzene}\\ \text{Used per kkg}\\ \text{of Styrene}\\ \text{Produced}\end{pmatrix} = \begin{matrix}\text{kkg of Benzene}\\ \text{Released}\\ \text{per kkg of}\\ \text{Benzene Used}\end{matrix}$$

$$(1.5 \times 10^{-3}) \qquad (0.84) \qquad = \qquad 1.8 \times 10^{-3}$$

Application of this release factor to 1978 benzene consumption for ethylbenzene and styrene synthesis gave:

$$\begin{pmatrix}\text{Benzene}\\ \text{Used}\end{pmatrix} \begin{pmatrix}\text{Release Factor}\\ \text{per Benzene}\\ \text{Used}\end{pmatrix} = \begin{matrix}\text{Benzene}\\ \text{Releases}\\ \text{to Air}\end{matrix}$$

$$(2.8 \times 10^{6}\ \text{kkg}) \qquad (1.8 \times 10^{-3}) \qquad = \qquad 5.1 \times 10^{3}\ \text{kkg}$$

The uncertainty of this value could not be independently evaluated.

A fourth estimate of a benzene release factor due to ethylbenzene/styrene synthesis was obtained by Hobbs and Key (1978). On the basis of site visits and industry responses to questionnaires, they estimated an overall release factor (including process, storage, fugitive, and secondary releases) of 1.17×10^{-3} kkg/kkg of styrene. This was converted to kkg/kkg of benzene as follows:

$$\begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of Styrene}\end{pmatrix} \div \begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Styrene}\end{pmatrix} = \begin{matrix}\text{Benzene Releases}\\ \text{per kkg}\\ \text{Benzene Used}\end{matrix}$$

$$(1.17 \times 10^{-3}) \qquad (0.84) \qquad = \qquad 1.4 \times 10^{-3}$$

Applying this release factor to 1978 benzene use for ethylbenzene/styrene synthesis yielded the following value for benzene releases to air during ethylbenzene/styrene synthesis:

$$\begin{pmatrix}\text{Benzene}\\ \text{Used}\end{pmatrix} \begin{pmatrix}\text{Benzene Releases}\\ \text{per kkg of Benzene}\\ \text{Used}\end{pmatrix} = \begin{matrix}\text{Benzene Releases}\\ \text{to Air}\end{matrix}$$

$$(2.81 \times 10^{6}\ \text{kkg}) \qquad (1.4 \times 10^{-3}) \qquad = \qquad 3.9 \times 10^{3}\ \text{kkg}$$

The uncertainty of the Hobbs and Key release factor could not be independently estimated, nor could the author of the report estimate the uncertainty because of the diversity of information sources that entered into the final value (Key, personal communication, 1980).

Of the four values for benzene releases to air, the 28,000 kkg estimate is an absolute maximum and is undoubtedly too high. By assuming either recycling or destruction of a large proportion of the unaccounted-for benzene, lower releases are estimated. The PEDCo and

Hobbs and Key release factors (the best-documented values) are in reasonable agreement. The latter release factor (Hobbs and Key 1978) is both more recent and more carefully documented by industry and site visit data. Therefore, the release amount derived from it has been used in the remainder of this report. It should be noted that this release factor is for uncontrolled releases, and thus represents a maximum estimate by Hobbs and Key.

5.3.1.3.2 Generated Releases to Water

Two estimates of benzene releases to water were found. These are summarized in Table 5.4. The amount of benzene generated for release to water was estimated to be 345 kkg in 1976 (Versar 1978). Ethylbenzene production that year was 1,790,000 kkg; the release factor was therefore:

$$\frac{\left(\begin{array}{c}\text{Benzene Released}\\ \text{to Water}\end{array}\right)}{\left(\begin{array}{c}\text{Ethylbenzene}\\ \text{Produced}\end{array}\right)} = \begin{array}{c}\text{kkg of}\\ \text{Benzene Released}\\ \text{per kkg of}\\ \text{Ethylbenzene Produced}\end{array}$$

$$\frac{(345\ \text{kkg})}{(1.79 \times 10^{6}\ \text{kkg})} = 1.9 \times 10^{-4}$$

Application of this release factor to 1978 ethylbenzene production yielded:

$$\left(\begin{array}{c}\text{Ethylbenzene}\\ \text{Produced}\end{array}\right)\left(\begin{array}{c}\text{Releases per}\\ \text{kkg of}\\ \text{Ethylbenzene}\\ \text{Produced}\end{array}\right) = \begin{array}{c}\text{Benzene Releases}\\ \text{to Water per kkg}\\ \text{of Ethylbenzene}\\ \text{Produced}\end{array}$$

$$(3.80 \times 10^{6}\ \text{kkg})\quad(1.9 \times 10^{-4}) = 720\ \text{kkg}$$

It was assumed that all effluent streams were subjected to secondary treatment, and that 47 percent of benzene was degraded by this process (Arthur D. Little, Inc., personal communication, 1980). The result was the following value for benzene released to receiving streams due to ethylbenzene synthesis in 1978:

$$\left(\begin{array}{c}\text{Benzene}\\ \text{Released}\\ \text{to Water}\end{array}\right)\left(\begin{array}{c}\text{Fraction}\\ \text{not}\\ \text{Removed}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\ \text{to Receiving}\\ \text{Streams}\end{array}$$

$$(720\ \text{kkg})\quad(0.53) = 380\ \text{kkg}$$

This value has an estimated uncertainty of ± a factor of 10, since it was based on estimates of both the overall release factor and the fraction of generated releases entering water. The main source of these water releases was probably scrubber effluents.

A second estimate of water releases during ethylbenzene/styrene synthesis was made by Hydroscience, Inc. (Hobbs and Key 1978). They

Table 5.4 Summary of Estimated Benzene Releases to Water Due to Ethylbenzene/Styrene Synthesis

Source of Estimate	Release Factor	Releases to Water, 1978 (kkg)	References
Industry estimates	1.9×10^{-4} kkg/kkg of ethylbenzene	380	Versar 1978
Site visits, industry estimates	8.0×10^{-5} kkg/kkg of ethylbenzene	120	Hobbs and Key 1978

estimated a factor of 6.7×10^{-5} kkg to liquid wastes (uncontrolled) per kkg of styrene. This is equal to:

$$\begin{pmatrix}\text{Benzene Releases}\\ \text{to Water per}\\ \text{kkg of Styrene}\end{pmatrix} \div \begin{pmatrix}\text{Benzene Used}\\ \text{per kkg}\\ \text{of Styrene}\end{pmatrix} = \begin{array}{c}\text{Benzene Releases}\\ \text{to Water per kkg}\\ \text{of Benzene Used}\end{array}$$

$$(6.7 \times 10^{-5}) \qquad (0.84) \qquad = \qquad 8.0 \times 10^{-5}$$

Applying this release factor to 1978 benzene consumption for ethylbenzene/styrene synthesis yielded the following value for benzene present in waste streams due to ethylbenzene:

$$(\text{Benzene Used}) \begin{pmatrix}\text{Releases per}\\ \text{kkg of}\\ \text{Benzene Used}\end{pmatrix} = \begin{array}{c}\text{Benzene in}\\ \text{Waste}\\ \text{Streams}\end{array}$$

$$(2.81 \times 10^{6}\ \text{kkg}) \qquad (8.0 \times 10^{-5}) \qquad = \qquad 220\ \text{kkg}$$

It was assumed that all waste streams were subjected to secondary treatment, and that 47 percent of benzene was degraded by this process (Arthur D. Little, Inc., personal communication, 1980). The resulting value for benzene released to receiving streams due to ethylbenzene synthesis in 1978 was as follows:

$$\begin{pmatrix}\text{Benzene in}\\ \text{Waste Streams}\end{pmatrix} \begin{pmatrix}\text{Fraction}\\ \text{not Removed}\end{pmatrix} = \begin{array}{c}\text{Benzene Released}\\ \text{to Receiving Streams}\end{array}$$

$$(220\ \text{kkg}) \qquad (0.53) \qquad = \qquad 120\ \text{kkg}$$

The uncertainty of this value could not be independently determined, nor could the author of the report estimate its uncertainty due to the diversity of information sources entering into the value (Key, personal communication, 1980).

Of the two estimates of water releases, the Hydroscience value (Hobbs and Key 1978) appears to be better documented by industry and site visit data. It will be used in the remainder of this report.

5.3.1.3.3 Releases Due to Disposal of Solid Residues

It was not possible to estimate releases of benzene in solid residues. In order to estimate these releases, it would be necessary to know: (1) the rate of production of benzene-containing sludges, (2) the percentage (by weight) of benzene in the sludge, and (3) the method of disposal of the sludge (landfill, incineration) Disposal of solid residues from ethylbenzene/styrene synthesis is estimated to be a relatively minor source of benzene releases.

5.3.1.3.4 Carry-Over of Benzene During Ethylbenzene/Styrene Synthesis

The possibility of benzene carry-over into ethylbenzene, styrene, and polystyrene was evaluated by a detailed literature search and by telephone communications with industry sources. Table 5.5 summarizes

Table 5.5 Carry-Over of Benzene into Ethylbenzene, Styrene, and Polystyrene

	Benzene $\xrightarrow{\text{99\% Yield}}$	Ethylbenzene $\xrightarrow{\text{90\% Yield}^{1}}$	Styrene $\longrightarrow$	Polystyrene
Amount Produced,[2] 1978 (kkg)	4.96×10^6	3.80×10^6	3.25×10^6	
Maximum benzene (weight %)		0.3 [3]	0.3 [4] 5×10^{-3} [5] 5×10^{-4} [7] 1×10^{-3} [9]	
Maximum residual benzene (kkg)		11,000 [3] 28,000 [10]	11,000 [4] 160 [5] 28,000 [4] 16 [7] 33 [9]	110 [4,8] 16 [5,8] 280 [4,8] 0.16 [7,8] 0.33 [9,8]

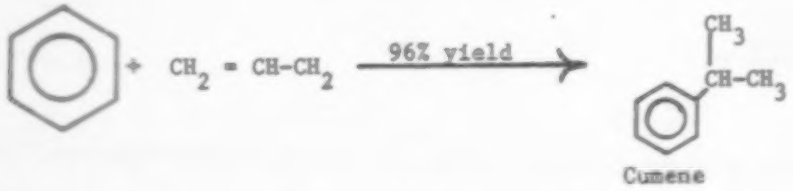
1. Hatch and Matar 1978
2. USITC 1979
3. Arthur D. Little, Inc. 1977
4. Assuming complete carry-over from ethylbenzene
5. Cosden Oil and Chemical Co., personal communication, 1980. Their limit is 50 ppm, but they feel the actual level is usually less than 10 ppm.
6. Some benzene may be reformed in this process
7. Gulf Oil Chemicals, personal communication, 1980. They specify a maximum benzene level of 5 ppm in their styrene monomer.
8. CFR Title 21, Parts 100-199, Section 177.1640 specifies 1 percent (w/w) residual styrene monomer in polystyrene and rubber-modified polystyrene for use in food packaging (FDA regulation).
9. Dow Chemical Co., personal communication, 1980. They estimate a maximum benzene concentration of 10 ppm in styrene monomer.
10. Based on unaccounted-for benzene (1 percent of 2.81×10^6 kkg).

these results. The values obtained from industry sources (i.e., analytical data) were judged to be the most reliable. Based on these values (16 to 160 kkg carried over into styrene), it appears that benzene contamination of polystyrene consumer products is minimal. Even the assumption of 1 percent styrene monomer in polystyrene appears to be a worst case estimate: analysis of commercial polystyrene yielded values in the range 0.06 to 0.36 percent styrene monomer (Seymour and McCormick 1978).

5.3.2 Consumption of Benzene by Cumene Synthesis

5.3.2.1 Processes, Producers, Locations

All chemical-grade cumene produced in the United States at present is made by the alkylation of benzene with propylene (Peterson 1979). The basic reaction in this process is:



Benzene and propylene are reacted at elevated temperatures and pressures in the presence of an acidic catalyst. In approximately 77 percent of cumene production the solid phosphoric acid (SPA) catalyst process is used; an aluminum chloride catalyst was used in the remaining production (Peterson 1979). A process flow diagram for the SPA process is shown in Appendix B-10. The producers of cumene, their locations, and production figures for 1978 are shown in Figure 5.2.

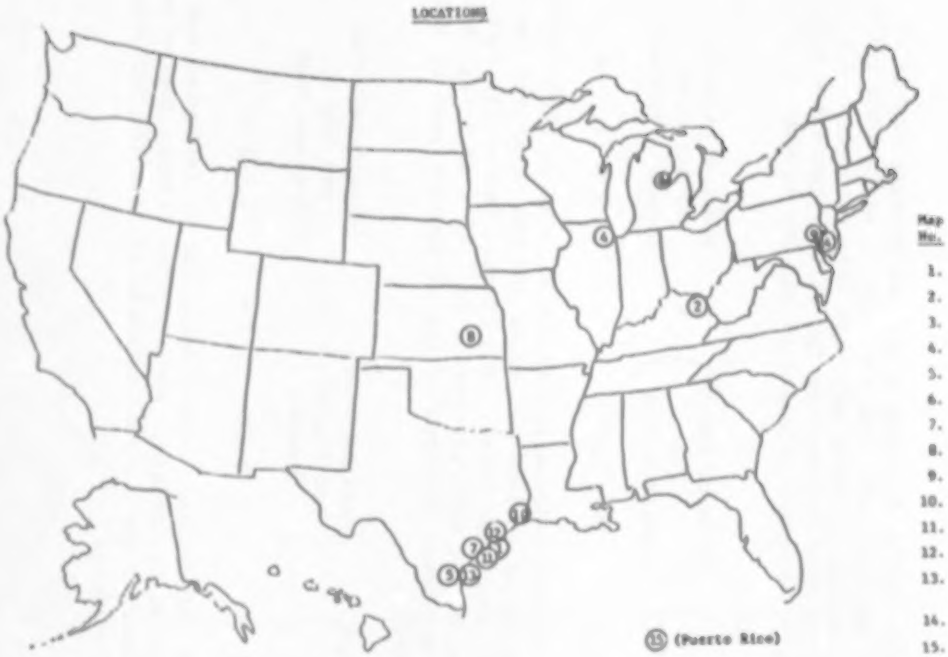
5.3.2.2 Amounts Manufactured

According to USITC (1979), 1,533,000 kkg of cumene were produced in 1978. The amount of benzene required to synthesize this amount of cumene was estimated by using the following conversion factor:

$$\frac{(\text{MW Benzene})}{(\text{MW Cumene})} \div \left(\begin{array}{c}\text{Theoretical}\\ \text{Yield}\end{array}\right) = \begin{array}{c}\text{Benzene Used}\\ \text{per kkg of Cumene}\end{array}$$

$$\frac{(78)}{(120)} \div (96\%) = 0.67$$

A 96 percent yield was estimated by Hatch and Matar (1978) for cumene synthesis. Applying this conversion factor to the USITC production data for cumene production yielded the following value for benzene required for:



Map No.	Company	Plant Location	Cumene Production, kkg
1.	Amoco Oil Co.	Texas City, TX	9,000
2.	Ashland Oil Co.	Catlettsburg, KY	122,000
3.	Chevron Oil Co.	El Segundo, CA	28,000
4.	Clark Oil Co.	Blue Island, IL	36,000
5.	Coastal States Gas Co.	Corpus Christi, TX	46,000
6.	Dow Chemical	Midland, MI	3,000
7.	Georgia Pacific Corp.	Houston, TX	229,000
8.	Getty Oil Co.	El Dorado, KS	41,000
9.	Gulf Oil	Philadelphia, PA	138,000
10.	Gulf Oil	Port Arthur, TX	135,000
11.	Monsanto Chemical Co.	Chocolate Bayou, TX	214,000
12.	Shell Oil Co.	Deer Park, TX	214,000
13.	Sun Petroleum Products Co.	Corpus Christi, TX	70,000
14.	Texaco., Inc.	Westville, NJ	46,000
15.	Union Carbide Corp.	Ponce, PR	196,000
	Total		1,530,000

Source: Peterson 1979. Total USITC cumene production was apportioned to individual plants according to their 1978 capacities.

Figure 5.2 Production of Cumene

$$(\text{Cumene Produced})\quad\begin{pmatrix}\text{Benzene Used}\\ \text{per kkg}\\ \text{of Cumene}\end{pmatrix} = \begin{matrix}\text{Benzene Used}\\ \text{in Cumene}\\ \text{Production}\end{matrix}$$

$$(1.533 \times 10^6 \text{ kkg})\quad(0.67) = 1.03 \times 10^6 \text{ kkg}$$

5.3.2.3 Releases of Benzene Due to Production of Cumene

5.3.2.3.1 Releases to Air

Several methods for estimating releases of benzene to air were applied to cumene synthesis. One of these also included releases due to subsequent production of phenol from cumene. These methods are summarized in Table 5.6.

Howard and Durkin (1974) estimated a maximum release by assuming that all benzene unaccounted for in the product may be released. Using an estimated yield of 96 percent benzene converted to cumene (Hatch and Matar 1978), an upper limit of 40,000 kkg can be placed on benzene releases.

Patterson et al. (1976) obtained a general release factor of 5×10^{-3} kkg/kkg of benzene used from the data in AP-42 (EPA 1977). It was not possible to assign an uncertainty to this estimate. Applying this release factor to 1978 benzene use for cumene production yielded the following value for benzene released to air due to cumene synthesis in 1978:

$$\begin{pmatrix}\text{Benzene Used in}\\ \text{Cumene Synthesis}\end{pmatrix}\quad\begin{pmatrix}\text{Release Factor}\\ \text{for}\\ \text{Benzene Used}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{to Air from}\\ \text{Cumene Synthesis}\end{matrix}$$

$$(1.03 \times 10^6 \text{ kkg})\quad(5 \times 10^{-3}) = 5 \times 10^3 \text{ kkg}$$

Two relevant benzene release factors were cited in PEDCo (1977): one for the conversion of benzene to cumene and the other for the subsequent oxidation of cumene to phenol. The release factor for cumene synthesis was reported by one manufacturer to be 2.45×10^{-4} kkg/kkg of cumene. This was expressed in terms of kkg of benzene used by the following conversion:

$$\begin{pmatrix}\text{Release Factor}\\ \text{per kkg of}\\ \text{Cumene}\end{pmatrix} \div \begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Cumene}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{per kkg of}\\ \text{Benzene Used}\end{matrix}$$

$$(2.45 \times 10^{-4})\quad(0.67) = 3.7 \times 10^{-4}$$

The uncertainty of this release factor could not be estimated due to lack of information on its origin. Applying the release factor to 1978 benzene consumption for cumene synthesis yielded the following value for benzene release:

Table 5.6 Summary of Estimated Benzene Releases to Air Due to Cumene/Phenol Synthesis

Source of Estimate	Benzene Release Factor (kkg per kkg of benzene used)	Releases to Air, 1978 (kkg)	Reference
Sum of unaccounted-for benzene	4×10^{-2}	4×10^{4}	Howard and Durkin 1974
Estimated release factor[1]	5×10^{-3}	5×10^{3}	Patterson et al. 1976
Industry estimate	3.7×10^{-4}	3.8×10^{2}	PEDCo 1977
Industry monitoring	1.5×10^{-3}(3)	1.3×10^{3}	PEDCo 1977
Site visits, industry estimate	1.9×10^{-3}	2.0×10^{3}	Peterson 1979[2]

1. Generalized from factors reported in AP-42 (EPA 1977).
2. See Appendix C for calculation of release factor.
3. Units: kkg/kkg of phenol (phenol synthesized from cumene).

$$\begin{pmatrix}\text{Benzene}\\ \text{Used}\end{pmatrix}\begin{pmatrix}\text{Benzene Released}\\ \text{per kkg of}\\ \text{Benzene Used}\end{pmatrix} = \begin{array}{c}\text{Benzene Released}\\ \text{to Air from}\\ \text{Cumene Synthesis}\end{array}$$

$$(1.03 \times 10^{6}\ \text{kkg}) \qquad (3.7 \times 10^{-4}) = 3.8 \times 10^{2}\ \text{kkg}$$

A factor for benzene release during conversion of cumene to phenol was also reported in PEDCo (1977). This value for uncontrolled releases, 1.5×10^{-3} kkg per kkg of phenol, was based on one manufacturer's stack monitoring data. It is probably at least an order of magnitude higher than representative controlled releases due to cumene oxidation, but its uncertainty is otherwise not known. Appyling this release factor to the 1978 phenol product as reported by USITC yielded the value for benzene released to air during cumene oxidation to phenol in 1978:

$$\begin{pmatrix}\text{Phenol}\\ \text{Produced}\end{pmatrix}\begin{pmatrix}\text{Benzene Released}\\ \text{per kkg of Phenol}\end{pmatrix} = \begin{array}{c}\text{Benzene Release}\\ \text{from Cumene}\\ \text{Oxidation to Phenol}\end{array}$$

$$(8.7 \times 10^{5}\ \text{kkg}) \qquad (1.5 \times 10^{-3}) = 1.3 \times 10^{3}\ \text{kkg}$$

An apparent inconsistency in these two stepwise release estimates is the result that the cumene synthesis step (in which benzene is used as a feedstock) releases less benzene than the cumene oxidation step (which has no obvious source of benzene). The release factor 1.5×10^{-3} kkg/kkg of phenol is based on data for only one of the nine plants studied (Pervier et al. 1974a). Release of benzene reportedly represented 15 percent of the total estimated hydrocarbon releases. Again, this does not seem reasonable for a process in which the only sources of benzene would be as a minor contaminant of the cumene feedstock or possibly as a product synthesized de novo in a minor side-reaction. Even the latter source can be discounted, since dealkylation is a reductive process and is thus not consistent with the major ongoing oxidative process.

The last release factor on Table 5.6 was derived from estimates of release factors from individual sources within a model cumene plant (Peterson 1979). The value obtained for uncontrolled releases (see Appendix C for calculations) was 1.9×10^{-3} kkg/kkg of benzene used. Applying this factor to 1978 benzene consumption for cumene synthesis yielded this value for benzene released to air due to cumene synthesis:

$$\begin{pmatrix}\text{Benzene Used}\\ \text{for}\\ \text{Cumene Synthesis}\end{pmatrix}\begin{pmatrix}\text{Benzene Released}\\ \text{per kkg of}\\ \text{Benzene Used}\end{pmatrix} = \begin{array}{c}\text{Benzene Released}\\ \text{to Air from}\\ \text{Cumene Synthesis}\end{array}$$

$$(1.03 \times 10^{6}\ \text{kkg}) \qquad (1.9 \times 10^{-3}) = 2.0 \times 10^{3}\ \text{kkg}$$

The uncertainty of this release factor could not be documented independently. The author believed that most of the estimates in the report were accurate to ±50%, but he could not estimate the uncertainty range for the individual release factors used (Peterson, personal communication, 1980).

Of the estimates presented in Table 5.6 for releases of benzene due to cumene/phenol synthesis, that by Hydroscience (Peterson 1979) was both the most recent and the best documented with regard to sources of information and assumptions used in the estimate. This value was therefore used in subsequent summaries in this report.

5.3.2.3.2 Releases to Water

Hydroscience, Inc., has estimated generated releases of benzene to water waste streams due to cumene synthesis for each of the two catalytic processes (Peterson 1979). A release factor was calculated by our using their estimated parameters (waste stream volume, benzene concentration). These calculations are presented below.

For the SPA process, Peterson (1979) estimated that a model cumene plant producing 227,000 kkg/year would generate an aqueous waste stream of 0.075 kkg/hour containing a volume of 0.002 kkg of benzene/kkg of water. The estimated parameters for the $AlCl_3$ process were: wastewater flow, 2.5 kkg/hour; and benzene concentration in wastewater, 0.002 kkg/kkg of water. The release factors were therefore:

$$\frac{\begin{pmatrix}\text{Water per}\\ \text{Hour}\end{pmatrix}\begin{pmatrix}\text{Conversion}\\ \text{Factors}\end{pmatrix}\begin{pmatrix}\text{Benzene}\\ \text{per kkg}\\ \text{of Water}\end{pmatrix}}{(\text{Cumene Produced})} = \begin{array}{c}\text{Benzene}\\ \text{Released}\\ \text{per kkg}\\ \text{of Cumene}\end{array}$$

SPA Process

$$\frac{(0.075\ \text{kkg/hr})\ (24\ \text{hr/day})\ (365\ \text{days/yr})\ (0.002)}{(2.27 \times 10^5\ \text{kkg/yr})} = 6 \times 10^{-6}$$

$AlCl_3$ Process

$$\frac{(2.5\ \text{kkg/hr})\ \ (24\ \text{hr/day})\ \ (365\ \text{days/yr})\ \ (0.002\ \text{kkg})}{(2.27 \times 10^5\ \text{kkg/yr})} = 2 \times 10^{-4}$$

By use of the Hydroscience estimate that 77 percent of production is by the SPA process and 23 percent is by $AlCl_3$ catalysis, the weighted average release factor was calculated as follows for all cumene-producing plants.

$$\left[\begin{pmatrix}\text{Fraction by}\\ \text{SPA Process}\end{pmatrix}\begin{pmatrix}\text{SPA}\\ \text{Release}\\ \text{Factor}\end{pmatrix}\right] + \left[\begin{pmatrix}\text{Fraction}\\ \text{by } AlCl_3\\ \text{Process}\end{pmatrix}\begin{pmatrix}AlCl_3\\ \text{Release}\\ \text{Factor}\end{pmatrix}\right] = \begin{array}{c}\text{Weighted Release}\\ \text{Factor per kkg}\\ \text{of Cumene}\end{array}$$

$$\left[(0.77)\ \ (6 \times 10^{-6})\right] + \left[(0.23)\ \ (2 \times 10^{-4})\right] = 5 \times 10^{-5}$$

Expressed in terms of benzene used by the following conversion:

$$\begin{pmatrix}\text{Weighted Release}\\ \text{Factor per kkg}\\ \text{of Cumene}\end{pmatrix} \div \begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Cumene}\end{pmatrix} = \begin{matrix}\text{Weighted Release}\\ \text{Factor per kkg}\\ \text{of Benzene}\end{matrix}$$

$$(5 \times 10^{-5}) \div (0.67) = 7 \times 10^{-5}$$

Applying this overall release factor to 1978 benzene consumption for cumene synthesis yielded the following value for benzene present in waste streams due to cumene synthesis in 1978.

$$\begin{pmatrix}\text{Benzene}\\ \text{Used}\end{pmatrix} \begin{pmatrix}\text{Weighted}\\ \text{Release Factor}\end{pmatrix} = \begin{matrix}\text{Benzene to}\\ \text{Waste Streams}\\ \text{from Cumene Production}\end{matrix}$$

$$(1.03 \times 10^{6} \text{ kkg}) \quad (7 \times 10^{-5}) = 70 \text{ kkg}$$

It was assumed that all waste streams were subjected to secondary treatment, and that 47 percent of benzene was degraded by this process (Arthur D. Little, Inc., personal communication, 1980). The resulting value for benzene released to receiving streams due to cumene synthesis in 1978 was as follows:

$$\begin{pmatrix}\text{Benzene to}\\ \text{Waste Streams}\\ \text{from Cumene}\\ \text{Production}\end{pmatrix} \begin{pmatrix}\text{Fraction}\\ \text{not}\\ \text{Removed}\end{pmatrix} = \begin{matrix}\text{Benzene to}\\ \text{Receiving Streams}\\ \text{from Cumene}\\ \text{Production}\end{matrix}$$

$$(70 \text{ kkg}) \quad (0.53) = 40 \text{ kkg}$$

The uncertainty of this estimate could not be independently evaluated. The author of the Hydroscience report thinks that most of the estimates in that report were accurate to ±50%, but he could not estimate the uncertainty range for the individual release factors used (Peterson, personal communication, 1980).

5.3.2.3.3 Releases Due to Disposal of Solid Residues

No information on the disposal of solid residues was provided. In order to estimate these emissions, it would be necessary to know: (1) the rate of formation of benzene-containing residues, (2) the percentage (by weight) of benzene in the residues, and (3) the method of residue disposal (incineration, landfill).

5.3.2.3.4 Carry-Over of Benzene Into Product

The amount of benzene carried over into cumene as a contaminant was evaluated by a literature search and by telephone interviews with industry sources. Table 5.7 summarizes the results. The analytical data from the industry sources were considered to be most reliable. From these values (7.5 to 15 kkg carried over into cumene), it appears that benzene contamination of cumene, phenol, and subsequent products is negligible.

Table 5.7 Carry-Over of Benzene into Cumene

	Benzene $\xrightarrow{96\% \text{ yield}^{1}}$	Cumene
Cumene produced, 1978 (kkg)	4.96	1.5×10^6
Maximum benzene (%, w/w)		0.1(3) 5×10^{-4}(4) 1×10^{-3}(5)
Maximum residual benzene (kkg)		1,500(3) 42,000(6) 7.5(4) 15(5)

1. Hatch and Matar 1978.
2. USITC 1979.
3. Interpretation of "Trace" in A.D. Little, Inc., 1977. The lowest concentration reported numerically in the source table was 0.1 percent.
4. Gulf Oil Chemicals, personal communication, 1980. They specify 5 ppm as the maximum benzene concentration in cumene.
5. Getty Oil, personal communication, 1980. They measure 0.001 percent benzene (v/v) in cumene. This also corresponds to 0.001 percent (w/w) because the densities are almost identical.
6. Based on unaccounted-for benzene: 4 percent of 1.06×10^6 kkg benzene used.

5.3.3 Consumption of Benzene by Cyclohexane Synthesis

5.3.3.1 Processes, Producers, Locations

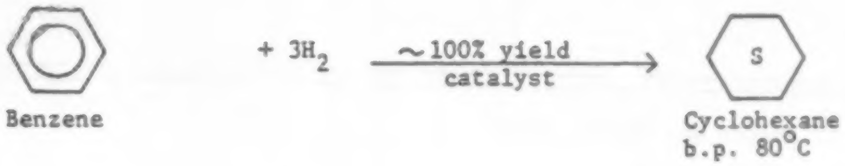
Three processes are used in the synthesis of cyclohexane:

1. Hydrogenation of benzene,
2. Isolation from crude gasoline by fractional distillation, and
3. Isolation from crude gasoline by fractional distillation with simultaneous isomerization (Weissermel and Arpe 1978).

Of these methods, hydrogenation of benzene accounted for 80 to 85 percent of cyclohexane production, while the other two accounted for the remaining 15 to 20 percent.

Hydrogenation of benzene produces cyclohexane of greater than 99 percent purity, as compared to 85 percent for the fractionating process and 98 percent for the fractionation combined with isomerization (A.D. Little, Inc. 1977).

The reaction equation for the catalytic hydrogenation of benzene is shown below.

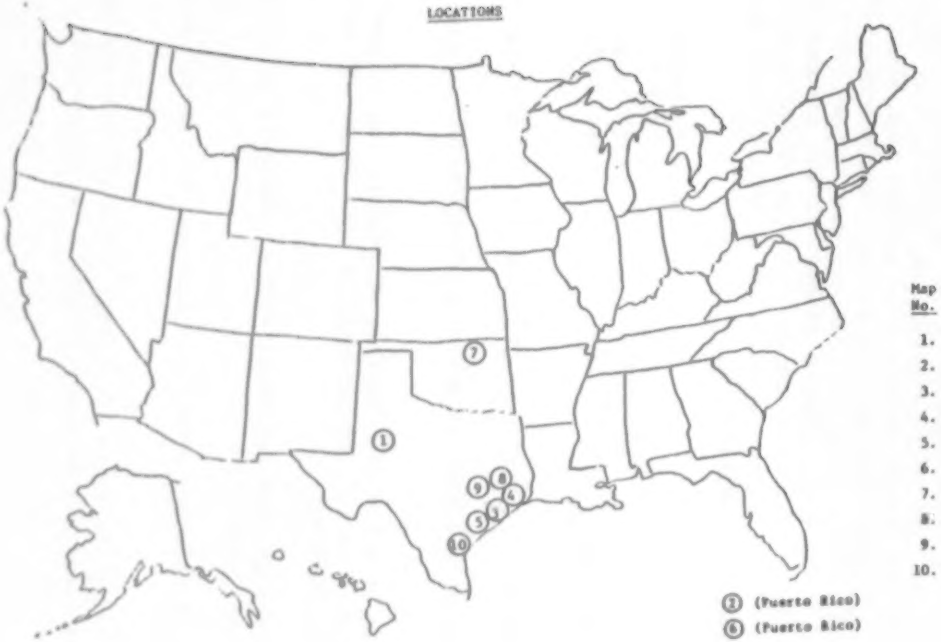


The process is carried out at elevated temperature in either liquid or vapor phase, at a hydrogen pressure of 20 to 40 atm. (Appendix B shows the industrial process flow chart for liquid-phase benzene hydrogenation.) Several reactors are used progressively to improve the conversion to cyclohexane until residual amounts of benzene and methylcyclopentane are reduced to less than 100 ppm (Weissermel and Arpe 1978).

Figure 5.3 shows the location of U.S. cyclohexane producers.

5.3.3.2 Amounts Produced

Production data for 1978 are also shown in Figure 5.3. The benzene requirement was calculated by using the conversion factor 0.93 kkg of benzene used per kkg of cyclohexane produced (Neufeld et al. 1978). Cyclohexane production by each plant in 1978 was estimated by assuming that the quantity produced was proportional to the fraction of the total U.S. production capacity that is contributed in 1976:



Map No.	Company	Plant Location	Cyclohexane Production[1] (kkg)
1.	American Petrofina	Big Springs, Tx	28,000
2.	Commonwealth Oil	Penuelas, PR	94,000
3.	Exxon Chemical	Baytown, TX	117,000
4.	Gulf Oil Chem.	Port Arthur, TX	84,000
5.	Phillips Chem.	Sweeny, TX	124,000
6.	Phillips Petroleum	Guayama, PR	169,000
7.	Sun Oil Co.	Tulsa, OK	66,000
8.	Texaco, Inc.	Port Arthur, TX	94,000
9.	Union Oil Calif.	Beaumont, TX	70,000
10.	Union Pacific	Corpus Christi, TX	52,000
		Total	898,000[2]

Source: SRI 1977

1. Derived from individual plant capacities (SRI 1977) using the assumption that a plant's percentage contribution to total production in 1978 equals its contribution to total capacity in 1976.
2. Equal to 85 percent of USITC production, the amount obtained by benzene hydrogenation.

Figure 5.3 Production of Cyclohexane

$$\begin{array}{c}\text{1978 Cyclohexane}\\\text{Production}\\\text{at Plant}\end{array} = \left(\begin{array}{c}\text{Total U.S.}\\\text{Production,}\\\text{1978}\end{array}\right)\left(\begin{array}{c}\text{Percent Total}\\\text{Capacity at}\\\text{Plant, 1976}\end{array}\right)$$

5.3.3.3 Benzene Releases Due to Cyclohexane Synthesis

5.3.3.3.1 Releases to Air

Benzene releases would be expected to be negligible during cyclohexane production from simple fractionation of natural gasoline (A.D. Little, Inc. 1977). This is because benzene is present only at trace levels as a minor constituent of the crude gasoline. The same analysis applies to the fractionation/isomerization method of cyclohexane synthesis.

Table 5.8 summarizes the release factors estimated by others for benzene releases to air during cyclohexane synthesis. A release factor of 2.8×10^{-3} kkg of benzene released per kkg of cyclohexane produced was cited by Mara and Lee (1978). They regarded it as an estimate accurate within an order of magnitude, and no information was presented on its origin. However, the release factor could not be greater than about 1×10^{-2} kkg/kkg of cyclohexane, because this is the maximum amount of benzene release consistent with a 99 to 100 percent cyclohexane yield. Since the factor was for benzene-consumption plants, it was assumed that it describes only the benzene hydrogenation process that accounts for 85 percent of cyclohexane production. Application of this release factor to 1978 cyclohexane production yielded:

$$\left(\begin{array}{c}\text{Cyclohexane}\\\text{Production}\\\text{1978}\end{array}\right)\left(\begin{array}{c}\text{Percent by}\\\text{Hydrogenation}\\\text{of Benzene}\end{array}\right)\left(\begin{array}{c}\text{Release}\\\text{Factor}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\\text{to Air from}\\\text{Cyclohexane}\\\text{Synthesis}\\\text{1978}\end{array}$$

$$(1.057 \times 10^{6}\ \text{kkg}) \quad (0.85) \quad (2.8 \times 10^{-3}) = 2{,}500\ \text{kkg}$$

A third release factor was that estimated by Hydroscience, Inc. (Blackburn 1978).

The estimated value of 3.2×10^{-4} kkg/kkg of product was derived in Appendix C from Blackburn's data. The assumptions upon which the calculation was based were as follows:

1. Model plant releases were representative of those by an actual plant of the same capacity.
2. Fifty percent of releases were controlled and 50 percent were uncontrolled.
3. Model plants using the (more efficient) internal floating-roof storage release controls were more relevant to the actual industry situation.

Table 5.8 Summary of Estimated Benzene Releases to Air Due to Cyclohexane Synthesis

Source of Estimate	Release Factor	Releases to Air, 1978 kkg	References
Sum of Unaccounted-for Benzene	1×10^{-2} kkg/kkg of benzene used	9,000	Hatch and Matar 1978
Not stated	2.8×10^{-3} kkg/kkg of product	2,500	Mara and Lee 1978
Site visits, industry estimates	3.2×10^{-4} kkg/kkg of product	290	Blackburn 1978

Calculation of benzene releases using the Hydroscience release factor yielded the following:

$$\begin{pmatrix}\text{Cyclohexane}\\ \text{Produced}\\ \text{1978}\end{pmatrix} \begin{pmatrix}\text{Percent by}\\ \text{Hydrogenation}\\ \text{of Benzene}\end{pmatrix} \begin{pmatrix}\text{Release}\\ \text{Factor}\end{pmatrix} = \begin{array}{l}\text{Benzene Release}\\ \text{from Cyclohexane}\\ \text{Production, 1978}\end{array}$$

$$(1.057 \times 10^{6} \text{ kkg}) \quad (0.85) \quad (3.2 \times 10^{-4}) = 290 \text{ kkg}$$

It was not possible to assign error limits to this estimate.

Of the three estimated releases, only the Hydroscience value is based on a documented release factor. Therefore, the Hydroscience estimate is used in this report.

5.3.3.3.2 Releases to Water

It has been qualitatively estimated that scrubber effluents - the main potential source of aqueous benzene releases - probably contain close to zero benzene because of the efficiency of the hydrogenation process (Blackburn 1978; Hydroscience, Inc., personal communication 1980).

5.3.3.3.3 Benzene Releases Due to Disposal of Solid Residues

Data concerning benzene releases due to disposal of solid wastes as a result of cyclohexane manufacture were not available. It was estimated qualitatively that during the regeneration of catalyst, no benzene was released (Blackburn 1978; Hydroscience, Inc., personal communication, 1980).

5.3.3.3.4 Carry-Over of Benzene into Product

Hydrogenation of benzene produces cyclohexane of more than 99 percent purity. Table 5.9 summarizes the estimates available on the amounts of benzene carried over into product cyclohexane. In view of the extreme efficiency of benzene hydrogenation, it would appear that the two highest estimates are less credible than the lower values. In fact, the estimate of 0.5 percent residual benzene is almost inconsistent with a 99 to 100 percent yield. Since the low estimates are judged to be reliable, we would conclude that the amount of benzene carried over into cyclohexane and its derivatives would be negligible.

While cyclohexane production from fractionation of crude gasoline and simultaneous isomerization has a 98 percent yield, neither the quantity of benzene residue nor its rate of release could be ascertained.

According to A.D. Little, Inc. (1977), the 15 percent of impurities in cyclohexane extracted from gasoline (Section 5.3.3.1) contained benzene, 2,2-dimethylpentane, and 2,4-diethylpentane. However, A.D. Little, Inc. (1977), also reported that the plant manager at the Borger, Texas, extraction plant stated in a personal communication that no benzene was present in the 85 percent cyclohexane end product. No information was available to resolve this conflict, nor has the possible release of these contaminants been studied.

Table 5.9 Carry-Over of Benzene into Cyclohexane

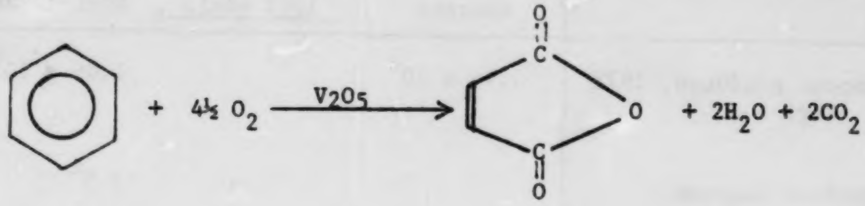
	Benzene	100% yield →	Cyclohexane
Amount produced, 1978 (kkg)	4.96×10^6		1.06×10^6
Maximum benzene (% by weight)			0.5[1]
			0.1[2]
			0.05[3]
			0.02 - 0.03[4]
			0.01[5]
			1×10^{-4}[6]
Maximum residual benzene (kkg)			5,300[1]
			1,100[2]
			530[3]
			210 - 320[4]
			110[5]
			1.1[6]

1. A.D. Little 1977.
2. Chevron Chemical, personal communication, 1980.
3. Exxon Chemical, personal communication, 1980.
4. Exxon Chemical, personal communication, 1980. According to Exxon, this is the benzene concentration above which cyclohexane becomes less reactive in subsequent nylon synthesis.
5. Weissermel and Arpe 1978.
6. Hancock 1975.

5.3.4 Consumption of Benzene by Maleic Anhydride Synthesis

5.3.4.1 Producers, Processes, Locations

In 1978, approximately 84 percent of maleic anhydride was produced by the catalytic oxidation of benzene (Gerry et al. 1979), according to the equation:



The yield was reported to be approximately 70 mole percent, with the other 30 mole percent being distributed among unreacted benzene (8 mole percent maximum), completely oxidized benzene (about 20 mole percent), and small amounts of other oxidation products (Kerr 1975). Appendix B shows the industrial process flow chart for benzene oxidation. The remaining 16 percent of maleic anhydride was synthesized by butane oxidation (15 percent) or isolated from phthalic anhydride waste streams (1 percent) (Gerry et al. 1979). Neither of these processes uses or releases benzene, and they are omitted in this report.

Figure 5.4 shows the locations and 1978 production of maleic anhydride producers.

5.3.4.2 Amounts Produced

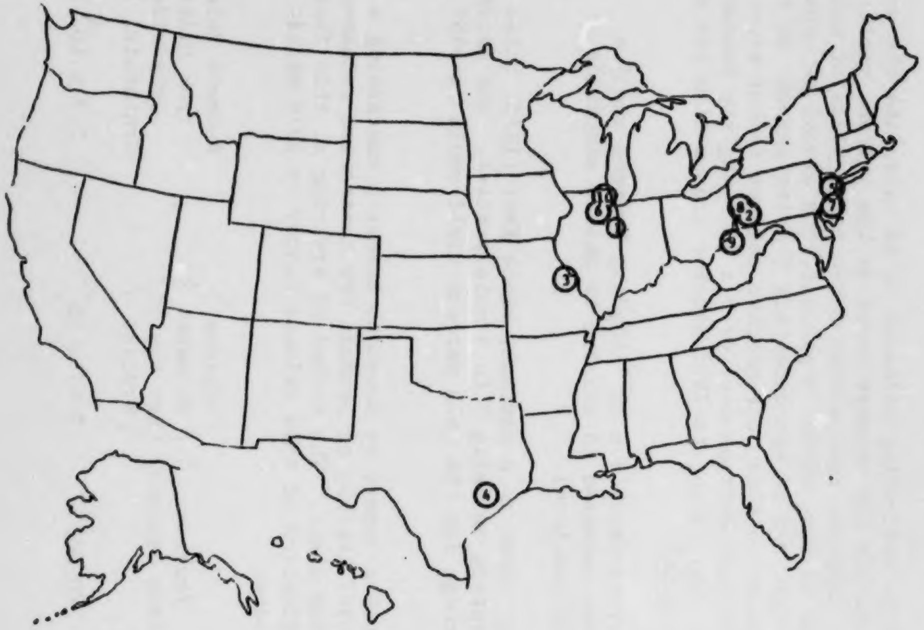
USITC reported a production of 155,000 kkg of maleic anhydride in 1978. The corresponding benzene requirement was estimated based on the following information:

1. Theoretically, 78 g of benzene yields 110 g of maleic anhydride.
2. In practice, a 70 percent molar yield is achieved (Kerr 1975).
3. Eighty-four percent of maleic anhydride is currently derived from benzene (Gerry et al. 1979).

The factor for conversion of maleic anhydride production to benzene consumption was as follows:

$$\frac{(\text{MW Benzene})\begin{pmatrix}\text{Fraction from}\\ \text{Benzene}\end{pmatrix}}{\begin{pmatrix}\text{MW Maleic}\\ \text{Anhydride}\end{pmatrix}\begin{pmatrix}\text{Percent}\\ \text{Yield}\end{pmatrix}} = \begin{matrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Maleic Anhydride}\\ \text{Processes}\end{matrix}$$

$$\frac{(78)(0.84)}{(110)(0.70)} = 0.85$$



Map No.	Company	Location	Maleic Anhydride Production, kkg[1]
1.	Amoco Chemical	Joliet, IL	15,000
2.	Koppers Co.	Bridgeville, PA	8,200
3.	Monsanto Co.	St. Louis, MO	26,000
4.	Denka Chemical	Houston, TX	13,000
5.	Reichold Chem.	Elizabeth, NJ	10,000
6.	Reichold Chem.	Morris, IL	15,000
7.	Tenneco, Inc.	Fords, NJ	6,600
8.	USS Chemicals	Neville Island, PA	19,000
9.	Ashland Oil	Neal, WV	15,000
10.	Koppers Co.	Cicero, IL	2,400
		Total	130,000

Source: Chemical Marketing Reporter 1978.

1. Maleic anhydride production due to benzene oxidation was equal to 84 percent of the annual production reported by USITC (1979). Benzene-derived maleic anhydride production was allocated to individual plants in proportion to their 1978 capacities.

Figure 5. 4 Production of Maleic Anhydride

Application of this conversion factor to 1978 maleic anhydride production yielded:

$$\left(\begin{array}{c}\text{Maleic Anhydride}\\ \text{Produced (USITC)}\end{array}\right)\left(\begin{array}{c}\text{Benzene}\\ \text{per kkg of}\\ \text{Maleic Anhydride}\end{array}\right) = \begin{array}{c}\text{Benzene Used for}\\ \text{Maleic Anhydride}\\ \text{Production, 1978}\end{array}$$

$$(1.55 \times 10^{5}\ \text{kkg}) \qquad (0.85) \qquad = \qquad 1.3 \times 10^{5}\ \text{kkg}$$

5.3.4.3 Releases Due to Maleic Anhydride Synthesis

5.3.4.3.1 Releases to Air

The main source of benzene releases during maleic anhydride synthesis was reported to be the condenser vent (labeled "to absorbers" in Appendix B) in the maleic anhydride recovery unit. Apparently the scrubbers are designed to capture maleic anhydride, but benzene is released directly at this point (Pervier et al. 1974a). Table 5.10 summarizes previously-reported factors for benzene releases to air, and the releases obtained from them.

A first approach to estimating releases is to calculate the maximum amount of benzene available for release based on the percent yield. The data cited in 5.3.4.1 indicate that although the molar yield of maleic anhydride from benzene is only about 70 percent, the amount of unoxidized benzene is not 30 percent but is approximately 8 molar percent of the feedstock benzene. Based on this, the maximum release factor expected would be 8×10^{-2} mole/mole benzene used or 8×10^{-2} kkg/kkg benzene used. Application of this factor to 1978 benzene consumption for maleic anhydride synthesis yielded:

> (130,000 kkg benzene used)(8×10^{-2} kkg/kkg benzene used) = 10,000 kkg benzene released to air due to maleic anhydride synthesis in 1978 (maximum).

This value is probably close to a maximum, since Kerr (1975) cited the range of unreacted benzene as being 3 to 8 mole percent. The corresponding uncertainty range for the mole percent yield would be +10%, -70%.

PEDCo (1977) cited a report by Monsanto Research containing a release factor of 0.0967 kkg/kkg of product for controlled releases from a maleic anhydride plant. The method of arriving at this factor was not stated. Application of this release factor to 1978 maleic anhydride production yielded:

$$\left(\begin{array}{c}\text{Maleic Anhydride}\\ \text{Sythesized, 1978}\end{array}\right)\left(\begin{array}{c}\text{Percent}\\ \text{from Benzene}\end{array}\right)\left(\begin{array}{c}\text{Benzene}\\ \text{Released}\\ \text{per kkg of}\\ \text{Product}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\ \text{from Maleic}\\ \text{Anhydride}\\ \text{Synthesis, 1978}\end{array}$$

$$(1.55 \times 10^{5}\ \text{kkg}) \qquad (0.84) \qquad (9.67 \times 10^{-2}) \qquad = \qquad 1.3 \times 10^{4}\ \text{kkg}$$

Table 5.10 Summary of Estimated Benzene Releases to Air Due to Maleic Anhydride Synthesis

Source of Estimate	Release Factor (kkg/kkg of product)	Releases to Air, 1978 (kkg)	Reference
Sum of unaccounted-for benzene	8×10^{-2}*	10,000	
Not stated	9.67×10^{-2}	13,000	Lewis and Hughes 1977, as cited in PEDCo 1977
Industry estimates (survey)	6.7×10^{-2}	8,700	Pervier et al. 1974a
Industry estimates, site visits	2.8×10^{-2}	3,600	Lawson 1978
Not stated	13.1×10^{-2}	17,000	Liepins et al. 1977

*kkg/kkg of benzene used.

It was not possible to estimate the uncertainty of this release value, due to lack of information on the release factor used.

Pervier et al. (1974a) carried out an inventory of maleic anhydride producers and estimated an overall release factor for benzene of 6.7×10^{-2} kkg/kkg of product, based on industry response to questionnaires. The factors reported ranged from 6×10^{-2} to 20×10^{-2} kkg/kkg of product. Application of the overall release factor to 1978 maleic anhydride production yielded:

$$\begin{pmatrix}\text{Maleic Anhydride}\\ \text{Synthesis, 1978}\end{pmatrix}\begin{pmatrix}\text{Percent}\\ \text{from Benzene}\end{pmatrix}\begin{pmatrix}\text{Benzene}\\ \text{Released}\\ \text{per kkg of}\\ \text{Product}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{from Maleic}\\ \text{Anhydride}\\ \text{Synthesis, 1978}\end{matrix}$$

$$(1.55 \times 10^{5}\ \text{kkg}) \quad (0.84) \quad (6.7 \times 10^{-2}) = 8.7 \times 10^{3}\ \text{kkg}$$

The uncertainty of this release could not be estimated because the uncertainties of the industry estimates were not reported.

Hydroscience, Inc., has presented data from which a benzene release factor to air from maleic anhydride synthesis could be calculated (Lawson 1978). They estimate, based on a report by Pervier (1974a) and their own site visits, that a plant producing 22,700 kkg/year would generate 0.1936 kkg of uncontrolled benzene releases per hour during an 8,000-hour year. An important contribution of the Hydroscience report is the estimate that releases are at present approximately 59 percent controlled by the industry. The representative release factor would be:

$$\frac{\begin{pmatrix}\text{Benzene}\\ \text{Release}\\ \text{per Hour}\end{pmatrix}\begin{pmatrix}\text{Hours/}\\ \text{Year}\end{pmatrix}\begin{pmatrix}\text{Fraction}\\ \text{Released}\end{pmatrix}}{\begin{matrix}\text{Maleic Anhydride}\\ \text{Production per Year}\end{matrix}} = \begin{matrix}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Maleic Anhydride}\end{matrix}$$

$$\frac{(0.1936\ \text{kkg/hr})(8 \times 10^{3}\ \text{hr/yr})(0.41)}{(2.27 \times 10^{4}\ \text{kkg/yr})} = 2.8 \times 10^{-2}$$

Application of this factor to 1978 maleic anhydride production from benzene yielded:

$$\begin{pmatrix}\text{Maleic Anhydride}\\ \text{from Benzene,}\\ \text{1978}\end{pmatrix}\begin{pmatrix}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Maleic Anhydride}\end{pmatrix} = \begin{matrix}\text{Benzene Release}\\ \text{from Maleic}\\ \text{Anhydride}\\ \text{Synthesis, 1978}\end{matrix}$$

$$(1.3 \times 10^{5}) \quad (2.8 \times 10^{-2}) = 3.6 \times 10^{3}\ \text{kkg}$$

It was not possible to assign an uncertainty to this estimate.

In a 1977 summary of industrial process profiles, Liepins et al. characterized the air waste stream of the recovery section scrubber as containing 13.1×10^{-2} kkg of benzene/kkg of product. The origin of this estimate was not discussed. Application of this release factor to 1978 maleic anhydride production yielded:

$$\begin{pmatrix}\text{Maleic}\\ \text{Anhydride}\\ \text{Produced}\end{pmatrix} \begin{pmatrix}\text{Fraction}\\ \text{from}\\ \text{Benzene}\end{pmatrix} \begin{pmatrix}\text{Benzene}\\ \text{Release}\\ \text{per kkg of}\\ \text{Product}\end{pmatrix} = \begin{matrix}\text{Benzene Release}\\ \text{from Maleic}\\ \text{Anhydride}\\ \text{Synthesis}\end{matrix}$$

$$(1.55 \times 10^{5} \text{ kkg}) \quad (0.84) \quad (13.1 \times 10^{-2}) = 1.7 \times 10^{4} \text{ kkg}$$

The uncertainty of this release estimate could not be evaluated. The value is significantly higher than the maximum permitted by stoichiometric considerations, and would thus appear to be an overestimate.

Of the five estimated release factors available, the Hydroscience factor is the most recent and also the best documented, since it takes into account the level of release control apparently practiced by industry (Lawson 1978). The estimated benzene release derived by using this factor was judged to be most representative, and will be used in the present report.

5.3.4.3.2 Releases to Water

The synthesis of maleic anhydride is of necessity an anhydrous process, since the anhydride would be hydrolyzed in the presence of process water. Thus, any loss of benzene to water would be indirect (scrubber effluents, leaks). Versar (1979) cited Versar (1978) as the source of an estimated aqueous release of 8 kkg in 1976 due to maleic anhydride synthesis. Consulting the latter source, however, failed to reveal any mention of benzene releases due to maleic anhydride synthesis. Thus, although the low estimated aqueous release was qualitatively reasonable, its origin was unclear. No uncertainty range was assigned to this value.

5.3.4.3.3 Releases Due to Disposal of Solid Residues

No data were available on benzene releases due to disposal of solid residues. The vacuum column waste stream would be expected to contain no benzene, because benzene has a lower boiling point than maleic anhydride and would exit the column with the product. From this brief analysis, it was estimated that releases of benzene due to disposal of solid residues from maleic anhydride synthesis were negligible.

5.3.4.3.4 Carry-Over of Benzene into Product

The possibility of carry-over of benzene into maleic anhydride product was assessed by telephone interviews with industry representatives. Table 5.11 summarizes the results. The analytical data from industry indicate that benzene carry-over into maleic anhydride is almost nonexistent.

Table 5.11 Carry-Over of Benzene into Maleic Anhydride

	Benzene	$\xrightarrow{\text{70\% yield}}$ Maleic anhydride
Amount produced, 1978(1) (kkg)	4.96×10^{6}	1.55×10^{5}
Maximum benzene (weight percent)		0.1(2) 1×10^{-3}(3) 1×10^{-3}(4)
Maximum residual benzene (kkg)		160(2) 2(3) 2(4)

[1] Source: USITC 1979.

[2] Interpretation of "Trace" in A.D. Little 1977. The lowest concentration reported numerically was 0.1 percent.

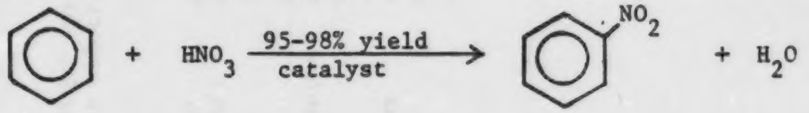
[3] Reichold Chemical Co., personal communication, 1980. They detect zero benzene in their product with a detectability level of 10 ppm.

[4] USS Chemicals, personal communication, 1980. They detect zero benzene in their product with a detectability level of 5 to 10 ppm.

5.3.5 Consumption of Benzene by Nitrobenzene Synthesis

5.3.5.1 Processes, Producers, and Locations

Synthesis of nitrobenzene is carried out by the nitration of benzene (Hatch and Matar 1978):



The process is carried out in liquid phase. Almost all nitrobenzene is used in the subsequent production of aniline (Klapproth 1979). Appendix B is a process flow diagram for nitrobenzene synthesis.

Figure 5.5 lists the nitrobenzene producers, plant locations, and estimated 1978 production by plant.

5.3.5.2 Amount of Benzene Consumed

In 1978, 170,000 kkg of benzene were used for the synthesis of nitrobenzene. This value was obtained by the operation:

$$\begin{pmatrix}\text{kkg of Nitrobenzene}\\ \text{Product}\end{pmatrix}\begin{pmatrix}\text{Conversion}\\ \text{Factor}\end{pmatrix} = \begin{matrix}\text{kkg of Benzene}\\ \text{Used}\end{matrix}$$

The conversion factor was 0.65 kkg of benzene used/kkg of nitrobenzene produced. This factor was equal to the ratio of molecular weights (benzene/nitrobenzene) divided by the percentage of theoretical yield. The latter was estimated to be 97 percent by Neufeld et al. 1978. Application of this conversion factor in the above equation yielded:

$$\begin{pmatrix}\text{Nitrobenzene}\\ \text{Produced}\end{pmatrix}\begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Nitrobenzene}\end{pmatrix} = \begin{matrix}\text{Benzene Used}\\ \text{for Nitrobenzene}\\ \text{Synthesis, 1978}\end{matrix}$$

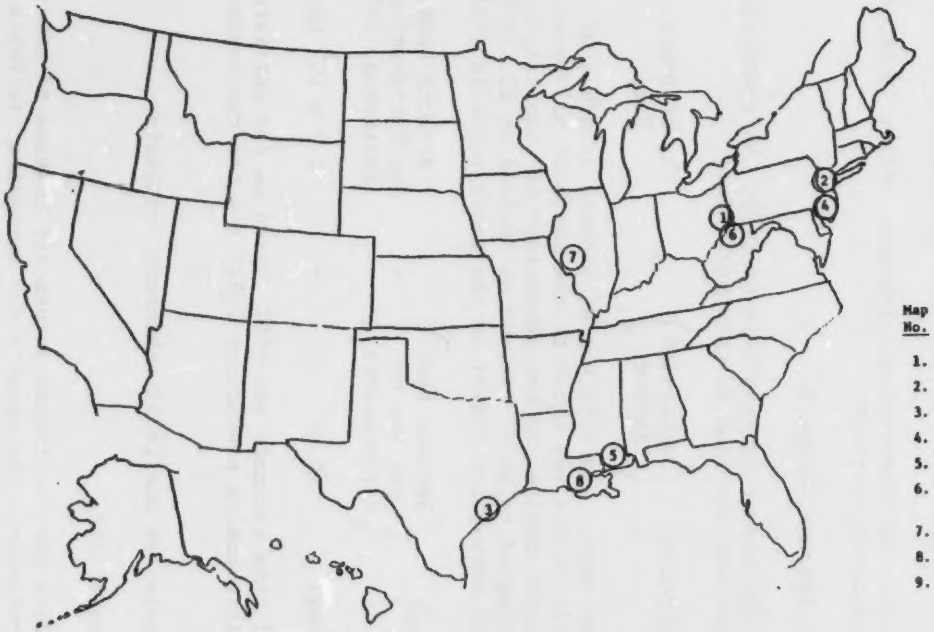
$$(2.61 \times 10^5 \text{ kkg}) \quad (0.65) = 1.7 \times 10^5 \text{ kkg}$$

The uncertainty of this estimate was ±20%, based on the estimated uncertainties of the nitrobenzene production (±5%) and the conversion factor (±15%).

5.3.5.3 Benzene Releases Due to Nitrobenzene Synthesis

5.3.5.3.1 Releases to Air

Previous studies have estimated values for release of benzene due to nitrobenzene synthesis. The results are summarized in Table 5.12.



Map No.	Company	Plant Location	Nitrobenzene Production, kkg
1.	Allied Chemical	Moundsville, WV	12,000
2.	American Cyanamid	Bound Brook, NJ	19,000
3.	E.I. duPont	Beaumont, TX	68,000
4.	E.I. duPont	Gibbstown, NJ	44,000
5.	First Mississippi Corp.	Pascagoula, MS	58,000
6.	Morbay Chemical	New Martinsville, WV	29,000
7.	Monsanto Co.	Sauget, IL	2,000
8.	Rubicon Chemicals	Geismar, LA	16,000
9.	American Cyanamid	Willow Island, WV	13,000
		Total	261,000

Source: Hobbs and Stuewe 1979. Total USITC nitrobenzene production was apportioned to individual plants according to their 1977 capacities. Not located: Willow Island, WV.

Figure 5.5 Production of Nitrobenzene

Table 5.12 Summary of Estimated Benzene Releases to Air Due to Nitrobenzene Synthesis

Source of Estimate	Release Factor (kkg/kkg of product)	Releases to Air, 1978 (kkg)	Reference
General release factor for benzene consumption	5×10^{-3}	900	Patterson et al. 1976
Measured releases at reactor vent	8.3×10^{-3}	2,200	Process Research, Inc. 1972
Release estimate plus production	1.8×10^{-2}	4,700	Cited in PEDCo 1977
Industry estimates, site visits	1.3×10^{-3}	340	Hobbs and Stuewe 1979

*kkg/kkg of benzene.

Patterson et al. (1976) may apply a release factor of 5×10^{-3} kkg/kkg (0.5 percent) to benzene-consuming processes. This value, in turn, is based on "available data in [Compilation of Air Pollutant Emission Factors, U.S. EPA Report AP-42, April 1973] and emission data for other similar processes." Applying this release factor to 1978 benzene use for nitrobenzene synthesis yielded:

$$\begin{pmatrix}\text{Benzene Used}\\ \text{in Nitrobenzene}\\ \text{Synthesis}\end{pmatrix}\begin{pmatrix}\text{Release}\\ \text{Factor}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{to Air During}\\ \text{Nitrobenzene}\\ \text{Synthesis}\end{matrix}$$

$$(1.7 \times 10^{5}\ \text{kkg}) \qquad (5 \times 10^{-3}) = 900\ \text{kkg}$$

Because of the lack of background information, it was not possible to evaluate the uncertainty of this release.

A second release estimate was derived from a factor of 8.3×10^{-3} kkg of benzene released to air per kkg of nitrobenzene produced (Process Research, Inc. 1972). This release factor was derived from measurements at the reactor absorber vent of a benzene nitration plant, and is characterized by the authors as being based on little or no census or experimental data. No uncertainty range was associated with the number. Application of the release factor to 1978 nitrobenzene production yielded:

$$\begin{pmatrix}\text{Nitrobenzene}\\ \text{Produced}\end{pmatrix}\begin{pmatrix}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Product}\end{pmatrix} = \begin{matrix}\text{Benzene Release}\\ \text{to Air During}\\ \text{Nitrobenzene}\\ \text{Synthesis}\end{matrix}$$

$$(2.61 \times 10^{5}\ \text{kkg}) \qquad (8.3 \times 10^{-3}) = 2.2 \times 10^{3}\ \text{kkg}$$

A third estimate was that of PEDCo (1977). These authors reported an estimate by Monsanto Research that 1975 benzene releases due to nitrobenzene synthesis totaled 3,390 kkg. The origin of this estimate was not discussed. Since 1975 nitrobenzene production (as reported by USITC) was 188,000 kkg, the release factor was:

$$\frac{\begin{pmatrix}\text{Benzene Releases}\\ \text{Due to Nitrobenzene}\\ \text{1975}\end{pmatrix}}{\begin{pmatrix}\text{Nitrobenzene Production}\\ \text{1975}\end{pmatrix}} = \begin{matrix}\text{Benzene Releases}\\ \text{per kkg of}\\ \text{Product}\end{matrix}$$

$$\frac{3.39 \times 10^{3}\ \text{kkg}}{1.88 \times 10^{5}\ \text{kkg}} = 1.8 \times 10^{-2}$$

Application of this release factor to 1978 nitrobenzene production (Table 5.1) yielded:

$$\left(\begin{array}{c}\text{1978 Nitrobenzene}\\ \text{Production}\end{array}\right)\left(\begin{array}{c}\text{Release}\\ \text{Factor}\end{array}\right) = \begin{array}{c}\text{Benzene Release}\\ \text{Due to Nitrobenzene}\\ \text{Synthesis, 1978}\end{array}$$

$$(2.61 \times 10^{5}\ \text{kkg}) \quad (1.8 \times 10^{-2}) = 4.7 \times 10^{3}\ \text{kkg}$$

No uncertainty range could be assigned to this value.

The fourth release factor listed was estimated by Hydroscience, Inc. (Hobbs and Stuewe 1979). It was based on industry responses to EPA's request for information, plus visits to two nitrobenzene/aniline plants. An important factor entering into the release value was the estimate that 50 percent of air releases in the nitrobenzene industry are controlled. Details of the calculation of the release factor are shown in Appendix C. Application of this factor to 1978 nitrobenzene production yielded:

$$\left(\begin{array}{c}\text{Nitrobenzene}\\ \text{Produced}\end{array}\right)\left(\begin{array}{c}\text{Release}\\ \text{Factor}\end{array}\right) = \begin{array}{c}\text{Benzene Released to}\\ \text{Air Due to}\\ \text{Nitrobenzene Synthesis}\end{array}$$

$$(2.61 \times 10^{5}\ \text{kkg}) \quad (1.3 \times 10^{-3}) = 3.4 \times 10^{2}\ \text{kkg}$$

It was not possible to assign an uncertainty range to this estimate.

Of the four estimated releases to air, the estimate by Hobbs and Stuewe is the most recent and also appears to be the best documented. Their estimate also takes into account the degree of emission control currently practiced by the industry. Their value is therefore taken as the best available estimate for the purposes of the present report.

5.3.5.3.2 Generated Releases to Water

Releases of benzene to aqueous streams were estimated. Table 5.13 summarizes the release factors obtained and the releases calculated from them.

Löwenbach and Schlesinger (1978) have reported a value for benzene concentration in the waste stream of a nitrobenzene/aniline plant. The estimate was based on data reported by two manufacturers. The average value obtained was 5×10^{-6} kkg of benzene/kkg of aniline; the range was 0 to 0.031×10^{-3} kkg/kkg of aniline. Data on the nitrobenzene process waste streams were apparently unavailable. Application of this average release factor to 1978 aniline production yielded:

$$\left(\begin{array}{c}\text{Aniline Produced}\\ \text{in 1978}\end{array}\right)\left(\begin{array}{c}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Aniline}\end{array}\right) = \begin{array}{c}\text{Benzene Release to}\\ \text{Water from Aniline}\\ \text{Synthesis, 1978}\end{array}$$

$$(2.61 \times 10^{5}\ \text{kkg}) \quad (5 \times 10^{-6}) = 1\ \text{kkg}$$

The uncertainty of this estimate was not reported. Even a 100-fold underestimate would leave this release small relative to estimated air releases during nitrobenzene synthesis.

Table 5.13 Summary of Estimated Benzene Releases to Water Due to Nitrobenzene Synthesis

Source of Estimate	Release Factor (kkg/kkg of product)	Releases to Water, 1978 (kkg)	Reference
Industry estimates	5×10^{-6}	1	Löwenbach and Schlesinger 1978
Site visits, physical parameters	1×10^{-4}	16	Hobbs and Stuewe 1978

Hobbs and Stuewe (1978) have estimated water releases of benzene due to nitrobenzene synthesis using the release factor 1×10^{-4} kkg/kkg of product. This factor was based on the following:

1. Benzene solubility, expressed in terms of the amount of water generated per unit of nitrobenzene synthesized, is 9.5×10^{-4} g/g of product at 25°C.

2. 90 to 95 percent of benzene was removed by steam stripping (Stuewe, personal communication, 1980).

Application of the release factor to 1978 nitrobenzene production yielded:

$$\begin{pmatrix}\text{Nitrobenzene}\\ \text{Produced}\end{pmatrix} \begin{pmatrix}\text{Release}\\ \text{Factor}\end{pmatrix} = \begin{matrix}\text{Benzene in}\\ \text{Raw Waste Streams}\end{matrix}$$

$$(2.61 \times 10^{5} \text{ kkg}) \quad (1 \times 10^{-4}) = 30 \text{ kkg}$$

It was further assumed that all waste streams were subjected to secondary treatment, and that this process removed 47 percent of the benzene (Arthur D. Little, Inc., personal communication, 1980). The amount of benzene released was then:

$$\begin{pmatrix}\text{Benzene in}\\ \text{Raw Waste}\\ \text{Streams}\end{pmatrix} \begin{pmatrix}\text{Fraction not}\\ \text{Removed}\end{pmatrix} = \begin{matrix}\text{Benzene Released to}\\ \text{Receiving Streams}\\ \text{from Nitrobenzene}\\ \text{Plants}\end{matrix}$$

$$(30 \text{ kkg}) \quad (0.53) = 16 \text{ kkg}$$

It was not possible to assign an uncertainty range to this estimate.

The magnitudes of these two estimates indicate that the vast majority of benzene releases are to the air.

5.3.5.3.3 Releases Due to Disposal of Solid Residues

No data were available that permitted estimation of benzene releases due to disposal of benzene-containing solid residues. In order to estimate these releases, it would be necessary to know:

1. The rate of production of benzene-containing sludges;

2. The percentage (by weight) of benzene in the sludge; and

3. The method of disposal of the sludge (landfill, incineration).

5.3.5.3.4 Carry-Over of Benzene into Nitrobenzene

The possibility of benzene carry-over into nitrobenzene or its major product, aniline, was investigated through a literature search and interviews with industry representatives. Table 5.14 summarizes the results. Based on the analytical data of the two manufacturers contacted, it appears that the amount of benzene carried over into aniline and consumer products made from aniline is negligible.

Table 5.14 Carry-Over of Benzene into Nitrobenzene and Aniline

	Benzene	$\xrightarrow{97\%\ \text{yield}^{1}}$ Nitrobenzene	$\xrightarrow{95\%\ \text{yield}^{1}}$ Aniline
Amount produced,[2] 1978, kkg	4.96×10^{6}	2.61×10^{5}	2.75×10^{5}
Maximum benzene (weight %)		3(3) 2×10^{-2}(4) 2×10^{-5}(6)	0.1(5) 5×10^{-4}(4) 0(6)
Maximum amount of residual benzene, kkg		7,800(3) 50(4) 0.05(6)	300(5) 1(4) 0(6)

1. Hatch and Matar 1978.
2. USITC 1979.
3. A.D. Little 1977.
4. First Chemical Corp., personal communication, 1980. They measure 200 ppm benzene in nitrobenzene and < 5 ppm in aniline.
5. Interpretation of "Trace" in A.D. Little 1977. The lowest concentration reported numerically is 0.1 percent.
6. American Cyanamid, personal communication, 1980. They find 0.2 ppm benzene in nitrobenzene and no benzene in aniline.

5.3.6 Consumption of Benzene by Chlorobenzene Synthesis

5.3.6.1 Processes, Production, Locations

In 1978, chlorobenzene proudction accounted for 0.3 percent of the total U.S. benzene consumption (Table 5.1). The three main commercial products obtained through the chlorination of benzene are monochlorobenzene, *ortho*-dichlorobenzene, and *para*-dichlorobenzene. Additional chlorination of these produces other polychlorobenzenes, e.g., 1,2,4-trichlorobenzene. Also, *meta*-dichlorobenzene is manufactured by the isomerization of *ortho*- or *para*-dichlorobenzene, but it is not covered in this report because benzene releases from the isomerization process would be expected to be very small.

Commercial benzene chlorination is done by two processes: batch or continuous (Arthur D. Little, Inc. 1977). These may be executed in the vapor phase for the production of monochlorobenzene, as is done by Dow, Midland, Michigan; but more generally the chlorination is carried out in the liquid phase (Arthur D. Little, Inc. 1977). Appendix B shows a process flow diagram for the manufacture of chlorobenzene. The equations for the chlorination of benzene are presented below:

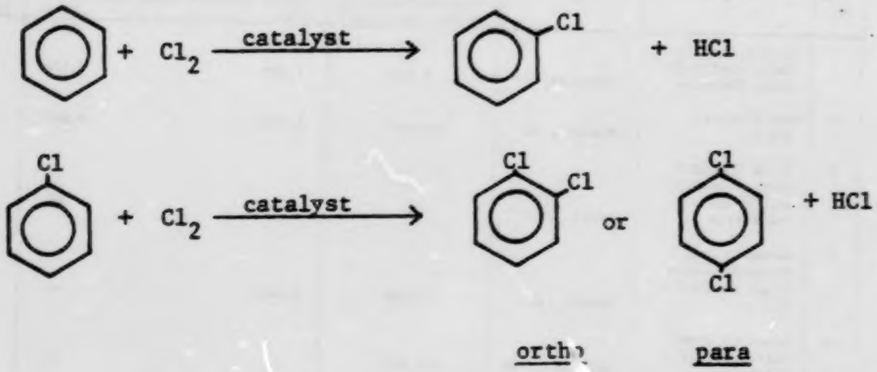
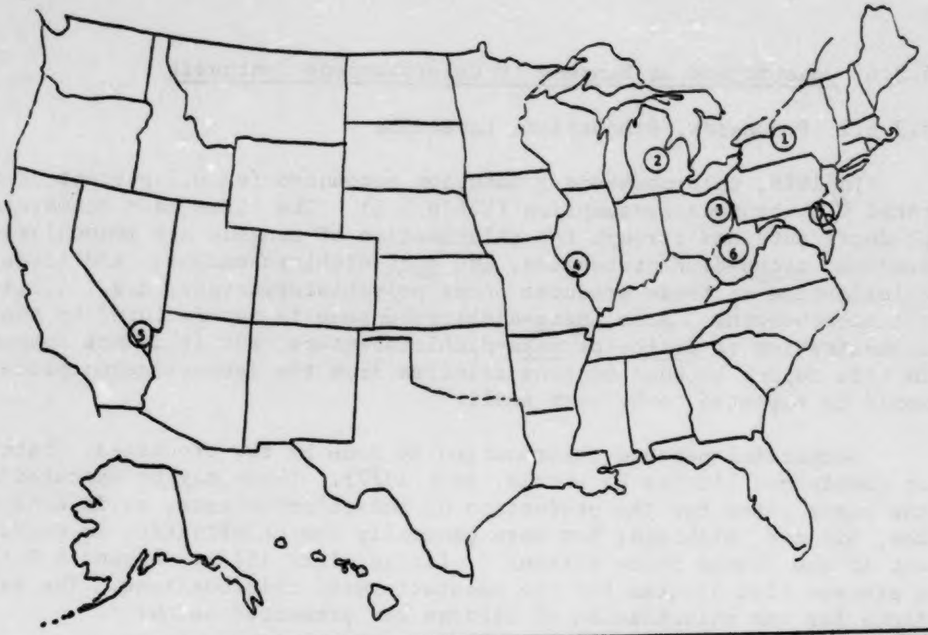


Figure 5.6 lists the producers of monochlorobenzene, *ortho*- and *para*-dichlorobenzene and their locations together with their respective 1978 production and corresponding benzene requirements. The listed production figures are reported to be subject to substantial change since the chemical processes involved are inherently easy to control in meeting demands for specific chlorobenzene isomers (Arthur D. Little, Inc. 1977). From the uncertainties of the USITC data (an estimated ±10%) and of the capacities (±20%), we believe that the 1978 production levels are subject to an uncertainty of ±30%. The benzene requirements were estimated by use of the following conversion factors (SRI 1977): 0.82 kkg of benzene used per kkg of monochlorobenzene produced; and 0.62 kkg of benzene used per kkg of *ortho*- or *para*-dichlorobenzene produced. The total benzene requirement for the three chlorobenzenes was estimated to be 130,000 kkg.



Map No.	Company[1]	Location	Estimated 1978 Monochlorobenzene Production (kkg)[2]	Estimated 1978 Dichlorobenzene Production (kkg)[2]		Benzene Requirement (kkg/yr)[3]
				Ortho	Para	
1	Allied Chem Corp. Industrial Chemicals Division	Syracuse, NY	4,800	1,700	2,100	6,300
2	Dow Chemical U.S.A.	Midland, MI	60,000	5,300	6,600	57,000
3	Dover Chemical Corp., Subsidiary of ICC Industries	Dover, OH	—	—	NA	NA
4	Monsanto Co., Monsanto Industrial Chemicals Co.	Sauget, IL	23,000	3,400	—	21,000
5	Montrose Chemical Corp. of California	Henderson, NV	14,000	—	—	11,000
6	PPG Industries, Inc., Chemical Division	Natrium, WV	18,000	—	—	15,000
7	Standard Chlorine Chemical Co., Inc.	Delaware City, DE	15,000	8,500	10,000	24,000
	TOTAL (USITC)		134,000	19,000	19,000	134,000

Notes:

NA = Not Available — = Not Manufactured

1. Source: USITC 1979.
2. USITC reported production was allocated among the producers according to their 1976 capacities as reported in SRI 1977.
3. Estimated using the conversion factors 0.82 kkg of benzene/kkg of monochlorobenzene produced, and 0.62 kkg benzene/kkg of *o*- or *p*-dichlorobenzene (SRI. 1977). The conversion factors are based on 85 percent yields of the respective chlorobenzenes from benzene.

Figure 5.6 Production of Chlorobenzene

5.3.6.2 Benzene Releases Due to Synthesis of Chlorobenzenes

5.3.6.2.1 Generated Releases to Air

Previous studies have proposed factors for benzene release to the air resulting from chlorobenzene synthesis. Table 5.15 summarizes these release factors and the benzene releases calculated from them.

Patterson et al. (1974) estimated a release factor of 5×10^{-3} to be applied to all benzene-using industrial processes. The factor was derived from an analysis of the release factors in AP-42 (an earlier version of EPA 1977). Application of the factor to 1978 benzene consumption for chlorobenzene synthesis yielded:

$$\begin{pmatrix}\text{Benzene Used for}\\ \text{Chlorobenzene}\\ \text{Synthesis}\end{pmatrix} \begin{pmatrix}\text{Release}\\ \text{Factor}\end{pmatrix} = \begin{matrix}\text{Benzene Released to}\\ \text{Chlorobenzene Synthesis}\end{matrix}$$

$$(1.34 \times 10^5 \text{ kkg}) \quad (5 \times 10^{-3}) = 7 \times 10^2 \text{ kkg}$$

The uncertainty of this release estimate could not be evaluated.

A second release factor was calculated from data cited by PEDCo (1977) as having been derived by Monsanto Research (1975). The method used by Monsanto was not reported, however. The factor was derived using Monsanto's total estimated releases due to chlorobenzene production in 1975 (2.286×10^3 kkg), the 1975 total chlorobenzene capacity (4.463×10^5 kkg), and the estimate that production was 50 percent of capacity in 1977 (and 1975) (Dylewski 1978). The release factor was calculated to be:

$$\frac{\begin{pmatrix}\text{Benzene Releases from}\\ \text{Chlorobenzene Production, 1975}\end{pmatrix}}{\begin{pmatrix}\text{Chlorobenzene}\\ \text{Capacity, 1975}\end{pmatrix}\begin{pmatrix}\text{Fraction of}\\ \text{Capacity}\end{pmatrix}} = \begin{matrix}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Chlorobenzene}\end{matrix}$$

$$\frac{(2.286 \times 10^3 \text{ kkg})}{(4.463 \times 10^5 \text{ kkg})(0.5)} = 1.0 \times 10^{-2}$$

Applying the release factor to 1978 chlorobenzene production yielded:

$$\begin{pmatrix}\text{Chlorobenzenes}\\ \text{Produced, 1978}\end{pmatrix} \begin{pmatrix}\text{Release}\\ \text{Factor}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{to Air from}\\ \text{Chlorobenzene Synthesis}\end{matrix}$$

$$(1.72 \times 10^5 \text{ kkg}) \quad (1.0 \times 10^{-2}) = 1.7 \times 10^3 \text{ kkg}$$

The uncertainty of this estimate could not be evaluated.

A third release factor was that of Hydroscience, Inc. (Dylewski 1978). This factor was based on industry responses to EPA requests for emissions data. Application of this factor to 1978 chlorobenzenes production yielded:

Table 5.15 Summary of Estimated Benzene Releases to Air Due to Chlorobenzenes Synthesis

Source of Estimate	Release Factor	Releases to Air, 1978 (kkg)	Reference
Estimated release factor (generalization from AP-42)	5×10^{-3} kkg/kkg of benzene used	700	Patterson et al. 1974
Not available	1.0×10^{-2} kkg/kkg of chlorobenzene produced (weighted average)	1,700	Monsanto Research 1975, as cited in PEDCo 1977
Industry survey	2.0×10^{-3} kkg/kkg of chlorobenzene produced	340	Dylewski 1978

$$\left(\begin{array}{c}\text{Chlorobenzenes}\\ \text{Produced, 1978}\end{array}\right)\left(\begin{array}{c}\text{Hydroscience}\\ \text{Release}\\ \text{Factor}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\ \text{to Air from}\\ \text{Chlorobenzene Synthesis}\end{array}$$

$$(1.72 \times 10^{5} \text{ kkg}) \quad (2.0 \times 10^{-3}) = 3.4 \times 10^{2} \text{ kkg}$$

The uncertainty of this release could not be estimated independently, nor could the author place uncertainty bounds on the release factor (Dylewski, personal communication).

Of the three values for benzene releases to air, the value of 340 kkg estimated by Hydroscience, Inc. (Dylewski 1978) was the only one based on industry data and site visits. Therefore, this value was used in subsequent sections of this report.

5.3.6.2.2 Benzene Releases to Water

A factor of 1.8×10^{-4} kkg of benzene released to water per kkg of chlorobenzenes synthesized has been reported by Hydroscience, Inc. (Dylewski 1978). This release factor was estimated using industry responses to an EPA request for information on releases, plus site visits and engineering judgments. Applying this release factor to 1978 chlorobenzene production yielded:

$$\left(\begin{array}{c}\text{Chlorobenzenes}\\ \text{Synthesized,}\\ \text{1978}\end{array}\right)\left(\begin{array}{c}\text{Water}\\ \text{Release}\\ \text{Factor}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\ \text{to Water from}\\ \text{Chlorobenzene Synthesis}\end{array}$$

$$(1.7 \times 10^{5} \text{ kkg}) \quad (1.8 \times 10^{-4}) = 31 \text{ kkg}$$

It was assumed that all waste streams were subjected to secondary treatment before leaving the plant, and that this process was 47 percent efficient in removing benzene (Arthur D. Little, Inc., personal communication, 1980). The amount of benzene released to receiving streams was as follows:

$$\left(\begin{array}{c}\text{Benzene to}\\ \text{Water from}\\ \text{Chlorobenzene}\\ \text{Production}\end{array}\right)\left(\begin{array}{c}\text{Fraction}\\ \text{not}\\ \text{Removed}\end{array}\right) = \begin{array}{c}\text{Benzene to}\\ \text{Receiving Streams}\\ \text{from Chlorobenzene}\\ \text{Synthesis}\end{array}$$

$$(31 \text{ kkg}) \quad (0.53) = 16 \text{ kkg}$$

It was not possible to estimate the uncertainty range of this release value, nor could the author of the Hydroscience report assign an uncertainty to the release factor (Dylewski, personal communication).

5.3.6.2.3 Benzene Releases Due to Disposal of Solid Residues

Neither qualitative nor quantitative data were available concerning benzene releases due to solid waste disposal as a result of chlorobenzene manufacture.

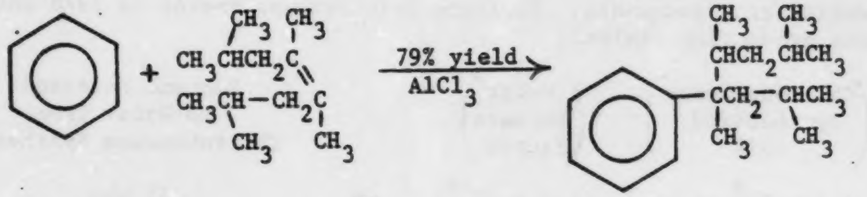
5.3.6.2.4 Carry-Over of Benzene as a Contaminant in Chlorobenzenes

Inherent in the processes used to manufacture chlorobenzenes is the possibility that these may be contaminated with benzene. We have attempted to evaluate this possibility by a literature search and interviews with industry sources. The results are summarized in Table 5.16. As judged from the fact that one of the major producers (Monsanto) reports a specification for maximum benzene concentration in its monochlorobenzene as 100 ppm, it would appear that the amount of benzene carried over into chlorobenzene and subsequent products is small.

5.3.7 Consumption of Benzene for Synthesis of Alkylbenzenes

5.3.7.1 Processes, Producers, and Locations

Alkylbenzenes (also called detergent alkylates and dodecylbenzenes) are formed by the alkylation of benzene with long-chain hydrocarbons. Use of branched dodecene as the alkylating agent yields branched chain dodecylbenzenes, while Fridel-Crafts alkylation with n-alkyl chlorides yields linear alkylbenzenes with 10- to 14-carbon chains (A.D. Little, Inc. 1977).


CH3 CH3
CH3CHCH2C
CH3CH—CH2C
CH3 CH3
79% yield
AlCl3
CH3 CH3
CHCH2CHCH3
CCH2—CHCH3
CH3 CH3

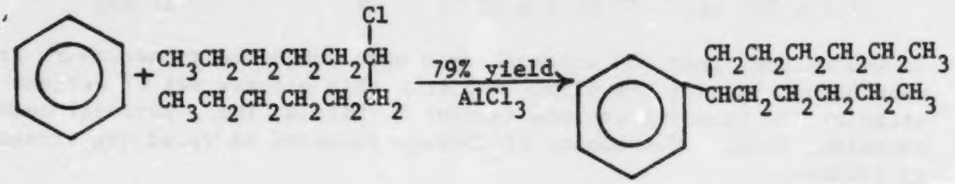

Cl
CH3CH2CH2CH2CH2CH
CH3CH2CH2CH2CH2CH2
79% yield
AlCl3
CH2CH2CH2CH2CH2CH3
CHCH2CH2CH2CH2CH3

Figure 5.7 shows the locations of alkylbenzene producers in 1978.

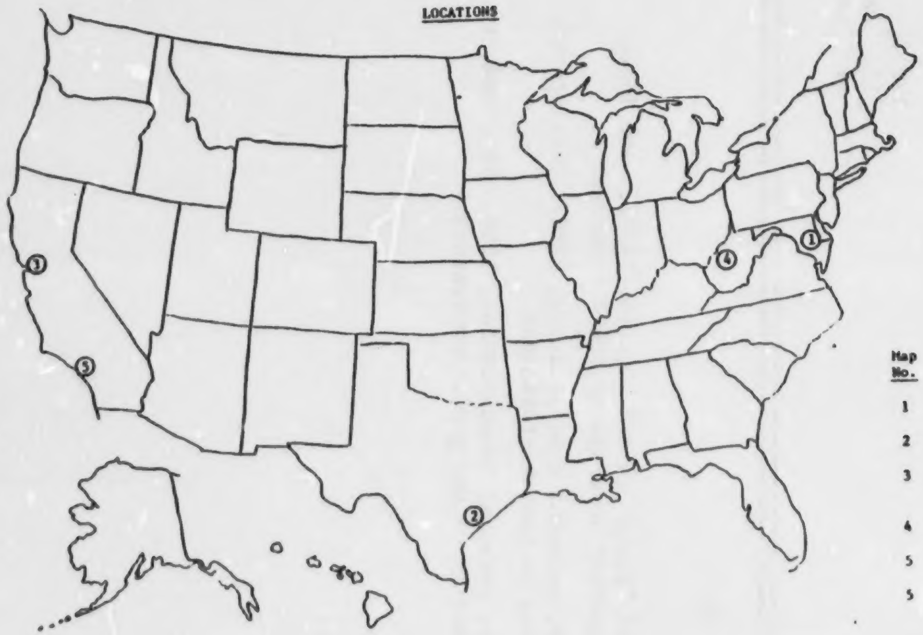
5.3.7.2 Amount Consumed

Figure 5.7 includes the alkylbenzene production for each producer and the total production: 330,000 kkg (linear plus branched). The amount of benzene consumed by alkylbenzene production was calculated using the conversion factor 0.40 kkg of benzene used per kkg of alkylbenzene produced for both linear and branched-chain alkylbenzenes (Neufeld et al. 1978). This yielded:

Table 5.16 Carry-Over of Benzene into Chlorobenzenes

	Benzene	$\xrightarrow[85\% \text{ yield (di-)}^{1}]{85\% \text{ yield (mono-)}^{1}}$	Chlorobenzenes
Amount produced, 1978[2] (kkg)	4.96×10^6		1.7×10^5
Maximum benzene (weight %)			0.1(3) 0.01(4) (mono-) 0.03(5) (di-)
Maximum residual benzene (kkg)			170(3) 17(4) (mono-) 51(5) (di-)

1. Neufeld et al. 1977.
2. USITC 1979.
3. Interpretation of "Trace" in A.D. Little (1977). The lowest concentration reported numerically was 0.1 percent.
4. Monsanto Company, personal communication, 1980. They specify ≤ 100 ppm benzene in monochlorobenzene.
5. Monsanto Company, personal communication, 1980. They specify ≤ 300 ppm benzene in *o*- and *p*-dichlorobenzene.



Map No.	Company	Location	Alkylbenzene Production (kkg)[1]
1	Continental Oil	Baltimore, MD	89,000 (L)
2	Monsanto Co.	Chocolate Bayou, TX	84,000 (L)
3	Standard Oil (Chevron)	Richmond, CA	82,000 (B)
4	Union Carbide	South Charleston, WV	52,000 (L)
5	Witco Chem.	Carson, CA	15,000 (L)
5	Witco Chem.	Carson, CA	9,000 (B)
			330,000

Sources: Bradley 1979; Chemical Marketing Reporter 1979.

1. Total alkylbenzene production (linear + branched) was derived from the 1978 production figure for linear alkylbenzenes (239,000 kkg) using the 1978 ratio of capacities for linear/branched = 2.63. The total was then allocated to individual plants in proportion to their capacities. L = Linear, B = branched.

Figure 5.7 Production of Alkylbenzene

$$\begin{pmatrix}\text{Aklylbenzene}\\ \text{Produced,}\\ \text{1978}\end{pmatrix}\begin{pmatrix}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Alkylbenzene}\end{pmatrix} = \begin{matrix}\text{Benzene Used}\\ \text{for Alkylbenzene}\\ \text{Synthesis, 1978}\end{matrix}$$

$$(3.3 \times 10^5\ \text{kkg}) \quad (0.4) = 1.32 \times 10^5\ \text{kkg}$$

Based on the relatively small uncertainties of both the production figure and the conversion factor, the uncertainty of the benzene consumption figure was placed at ±30%.

5.3.7.3 Benzene Releases Due to Alkylbenzene Synthesis

5.3.7.3.1 Releases to Air

PEDCo (1977) cited a report of a personal communication between EPA and Union Carbide as the source of a release factor for controlled benzene release from a linear alkylation process: 5×10^{-4} kkg/kkg of product. No data were available on synthesis of branched alkylbenzenes. Because of the chemical similarity between the two synthesis reactions, it was assumed that the release factor for the linear alkylbenzene also applied to the branched alkylbenzene. Application of this release factor to 1978 alkylbenzene production yielded:

$$\begin{pmatrix}\text{Alkylbenzenes}\\ \text{Produced}\end{pmatrix}\begin{pmatrix}\text{Benzene Release}\\ \text{per kkg of}\\ \text{Alkylbenzene}\end{pmatrix} = \begin{matrix}\text{Benzene Release}\\ \text{to Air from}\\ \text{Alkylbenzene Synthesis}\end{matrix}$$

$$(3.3 \times 10^5\ \text{kkg}) \quad (5 \times 10^{-4}) = 1.7 \times 10^2\ \text{kkg}$$

5.3.7.3.2 Releases to Water

Hydroscience, Inc., presented data that permitted estimation of water releases of benzene due to alkylbenzene synthesis (Peterson 1978). In considering the chlorinated paraffin process for linear alkylbenzene synthesis, the author reported that about 0.4 kg of benzene/kkg of product was lost to effluent streams. This factor was applied to linear alkylbenzene production by Continental Oil, Union Carbide, and Witco (Figure 5.7), all of which use this process. The result was:

$$\begin{pmatrix}\text{Linear}\\ \text{Alkylbenzene}\\ \text{Production}\end{pmatrix}\begin{pmatrix}\text{Benzene Release}\\ \text{to Water per kkg}\\ \text{of Product}\end{pmatrix} = \begin{matrix}\text{Benzene to Water}\\ \text{from Alkylbenzene}\\ \text{Production}\end{matrix}$$

$$(1.56 \times 10^5\ \text{kkg}) \quad (4 \times 10^{-4}) = 60\ \text{kkg}$$

It was assumed that all waste streams were subjected to secondary treatment, and that 47 percent of benzene was degraded by this process (Arthur D. Little, Inc., personal communication, 1980). Thus, the amount of benzene released to receiving streams as a result of linear alkylbenzene synthesis by the chlorination paraffin process in 1978 was:

$$\begin{pmatrix}\text{Benzene to Water}\\ \text{from Alkylbenzene}\\ \text{Production}\end{pmatrix}\begin{pmatrix}\text{Fraction not}\\ \text{Degraded}\end{pmatrix} = \begin{matrix}\text{Benzene to}\\ \text{Receiving}\\ \text{Streams}\end{matrix}$$

$$(60\ \text{kkg}) \qquad (0.53) \qquad = \qquad 32\ \text{kkg}$$

It was not possible to assign uncertainty bounds to this release estimate.

Peterson (1978) also reported that 17.5 kg of benzene per day are released in waste streams during linear alkylbenzene synthesis by the olefin method in a plant reducing 90,000 kkg/year. Branched alkylbenzenes are also synthesized by an internal olefin process. Therefore, the release factor was applied to branched alkylbenzene production as well as to linear alkylbenzene production by Monsanto (which uses the olefin process). The result was:

$$\frac{\begin{pmatrix}\text{Benzene Release}\\ \text{per day}\end{pmatrix}\begin{pmatrix}\text{Conversion}\\ \text{Factors}\end{pmatrix}}{\begin{pmatrix}\text{Alkylbenzene}\\ \text{Produced per Year}\end{pmatrix}} = \begin{matrix}\text{Benzene Release}\\ \text{to Waste Streams}\\ \text{per kkg of}\\ \text{Alkylbenzene}\end{matrix}$$

$$\frac{(17.5 \times 10^{-3}\ \text{kkg/day})(1\ \text{day/24 hr})(8{,}000\ \text{hr/yr})}{(9 \times 10^{4}\ \text{kkg/yr})} = 6 \times 10^{-5}$$

Application of this factor is alkylbenzene synthesis by the olefin process (derived from Figure 5.7) yielded:

$$\begin{pmatrix}\text{Alkylbenzene}\\ \text{Synthesis}\end{pmatrix}\begin{pmatrix}\text{Benzene Release}\\ \text{to Waste Streams}\\ \text{per kkg of}\\ \text{Alkylbenzene}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{to Waste Streams}\end{matrix}$$

$$(1.75 \times 10^{5}\ \text{kkg}) \qquad (6 \times 10^{-5}) \qquad = \qquad 10\ \text{kkg}$$

It was assumed that all waste streams were subjected to secondary treatment, and that 47 percent of benzene was degraded by this process (Arthur D. Little, Inc., personal communication, 1980). The result value for benzene released to receiving streams due to alkylbenzene synthesis by the olefin process in 1978 was:

$$\begin{pmatrix}\text{Benzene Released}\\ \text{to Waste Streams}\\ \text{from Olefin Process}\end{pmatrix}\begin{pmatrix}\text{Fraction}\\ \text{not}\\ \text{Degraded}\end{pmatrix} = \begin{matrix}\text{Benzene Released}\\ \text{to}\\ \text{Receiving Streams}\end{matrix}$$

$$(10\ \text{kkg}) \qquad (0.53) \qquad = \qquad 5\ \text{kkg}$$

The sum of these releases to water, 35 kkg, was small compared to the estimated releases to air. It was not possible to estimate an uncertainty range for the value for aqueous releases.

5.3.7.3.3 Releases Due to Disposal of Solid Residues

Releases due to solid residue disposal were included in the estimate of releases to air (5.3.7.3.1).

5.3.7.3.4 Carry-Over of Benzene into Product

The possibility of benzene carry-over into alkylbenzene product was evaluated by telephone interviews with an industry representative. The results are shown in Table 5.17. Based on the information from the producer, benzene carry-over into alkylbenzenes appears to be negligible.

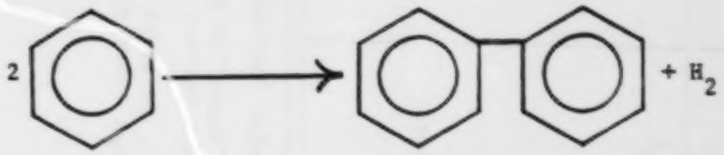
5.3.8 Consumption of Benzene by Synthesis of Anthraquinone

The Level I report on benzene indicated, on the basis of readily available information, that anthraquinone was one of the minor products synthesized from benzene. However, a spokesman for the sole U.S. producer of anthraquinone (Toms River Chemical Co., Toms River, New Jersey) stated that they now make anthraquinone from anthracene and use no benzene feedstock. Furthermore, he knew of no one else making anthraquinone by any method (Toms River Chemical Co., personal communication, 1980). Therefore, anthraquinone synthesis as a source of benzene releases is omitted from this Level II report.

5.3.9 Consumption of Benzene by Synthesis of Biphenyl

5.3.9.1 Processes, Producers, Locations

Thirty percent of total biphenyl production is directly from benzene by the thermal reaction of benzene vapors (Meylan and Howard 1976). Benzene feedstock is not used for the remaining yearly biphenyl production. The basic reaction for biphenyl synthesis from benzene is:



An industrial process flow diagram is shown in Appendix B. Benzene and the recycled benzene are vaporized, heated to about 600°C, and injected into a thermal reactor at 1 to 2 atm pressure. The reactor raises the temperature to 700° to 850°C; the time of exposure to the higher temperatures is about 1 second (Meylan and Howard 1976). Biphenyl was produced by this process only at the Anniston, Alabama, plant of Monsanto Industrial Chemicals Co.

Table 5.17 Carry-Over of Benzene into Alkylbenzenes

	Benzene $\xrightarrow[\text{catalyst}]{\text{79\% yield}}$	Alkylbenzenes
Amount produced, 1978[1] (kkg)	4.96×10^{6}	3.3×10^{5}
Maximum benzene (weight %)		0.1[2] 5×10^{-5} [3]
Maximum residual benzene (kkg)		330[2] 0.17[3]

1. USITC 1979. See also footnote 5, Table 5.1
2. Interpretation of "Trace" in A.D. Little (1977). The lowest concentration reported numerically was 0.1 percent.
3. Continental Oil Co., personal communication, 1980. They detect no benzene in their alkylbenzene with a lower detectability limit of 0.5 ppm.

5.3.9.2 Amounts Manufactured

According to USITC, 29,000 kkg of biphenyl were produced in 1978. From the 30 percent figure given in Meylan and Howard (1976) for the fraction of biphenyl produced from benzene, the amount of biphenyl produced by this method is 8,700 kkg.

5.3.9.3 Releases of Benzene Due to Production of Biphenyl

5.3.9.3.1 Releases to Air

Data on releases for 1978 were not found in any available sources. From 1976 benzene completion and release data for other nonfuel uses of benzene (Versar 1979), a release factor was calculated to be:

$$\frac{\text{Benzene Released}}{\text{Benzene Consumed}} = \text{Benzene Released per kkg Consumed}$$

$$\frac{(2 \times 10^{2} \text{ kkg})}{(3.4 \times 10^{4} \text{ kkg})} = 5.9 \times 10^{-3}$$

Using the benzene conversion factor given by Meylan and Howard (1976) of 0.08 kkg of benzene used per kkg of biphenyl produced, benzene consumption in the production of biphenyl was calculated to be:

$$\left(\begin{array}{c}\text{Biphenyl from}\\ \text{Benzene, 1978}\end{array}\right)\left(\begin{array}{c}\text{Benzene Used}\\ \text{per kkg of}\\ \text{Biphenyl}\end{array}\right) = \begin{array}{c}\text{Benzene Used}\\ \text{in Biphenyl}\\ \text{Synthesis, 1978}\end{array}$$

$$(8.7 \times 10^{3} \text{ kkg}) \quad (0.8) = 7 \times 10^{3} \text{ kkg}$$

Based on these calculations, benzene releases were estimated to be:

$$\left(\begin{array}{c}\text{Benzene Used}\\ \text{in Biphenyl}\\ \text{Synthesis, 1978}\end{array}\right)\left(\begin{array}{c}\text{Benzene Release}\\ \text{per kkg}\\ \text{Consumed}\end{array}\right) = \begin{array}{c}\text{Benzene Released}\\ \text{from Biphenyl}\\ \text{Synthesis, 1978}\end{array}$$

$$(7 \times 10^{3} \text{ kkg}) \quad (5.9 \times 10^{3} \text{ kkg}) = 41 \text{ kkg}$$

From the estimated uncertainties of the 1976 benzene release value for other nonfuel uses (± a factor of 2) and the conversion factor for benzene used per kkg of biphenyl (±20%) we estimated the cumulative uncertainty of the benzene releases in 1978 to be ± a factor of 3.

5.3.9.3.2 Releases to Water

No data were available on release factors or releases of benzene to water due to biphenyl synthesis. Because of the temperature and anhydrous nature of the process, aqueous releases would be expected to be small (probably due solely to scrubber streams). Further data are needed to confirm this qualitative evaluation.

5.3.9.3.3 Releases Due to Disposal of Solid Residues

According to Meylan and Howard (1976), the only wastes from the biphenyl process are the crude still pot residues. It is likely that a small amount of benzene will be present in these residues; however, no data were available to permit estimation.

5.3.9.3.4 Carry-Over of Benzene into Product

The possibility of carry-over of benzene into biphenyl was evaluated by contacting the sole U.S. producer using benzene feedstock: Monsanto Company, Anniston, Alabama. A Monstanto representative reported that they routinely monitor for benzene and observe no benzene with a lower detectability limit of 10 ppm (Monsanto Co., personal communication, 1980). Application of this maximum benzene concentration to 1978 production yielded:

$$\left(\begin{array}{c}\text{Biphenyl from}\\\text{Benzene, 1978}\end{array}\right)\left(\begin{array}{c}\text{Maximum}\\\text{Benzene}\\\text{Concentration}\end{array}\right) = \begin{array}{c}\text{Maximum Benzene}\\\text{Carry-Over}\\\text{in Biphenyl}\end{array}$$

$$(8.7 \times 10^{3}\ \text{kkg}) \quad (1 \times 10^{-5}) = 9 \times 10^{-2}\ \text{kkg}$$

Benzene carry-over into biphenyl is apparently not a potential source of significant population exposure.

5.3.10 Benzenesulfonic Acid

Benzenesulfonic acid was formerly a direct consumptive use of benzene, used only in the production of phenol. According to Neufeld et al. (1978), Reichold Chemicals, the only company producing phenol by the benzenesulfonic acid method, closed its plant in 1978. It was not possible to estimate releases for previous years.

5.3.11 Exports of Benzene

5.3.11.1 Amount Exported

Data provided by the Bureau of the Census (personal communication, 1980) indicated that 151,000 kkg of benzene were exported in 1978. The 1979 figure, extrapolated from January-October preliminary figures, was 68,000 kkg.

5.3.11.2 Releases Due to Benzene Export

Releases due to export were considered to be attributable to transport plus dockside loading. Release factors for these processes, estimated by PEDCo (1977), were applied to the export value (above). The results are summarized in Table 5.18. Total estimated releases were 17 kkg.

Of the total releases estimated for export, 90 percent were believed to go to air and 10 percent to water. These estimates were used because the only significant releases were those due to transport; most spill

Table 5.18 Release Factors and Releases Due to Benzene Export, 1978[1]

(Source: PEDCo 1977)

Process	Release Factor (kkg/kkg)	Releases[1] (kkg)
Benzene transport	1.1×10^{-4} /week	17.0
Benzene loading	6.9×10^{-8}	0.01
		Sum: 17.0

1. The average time in transit was estimated to be 1 week.

losses would be over land, and the benzene would evaporate before reaching water. Fugitive losses would be mostly evaporation during transfers.

Application of this breakdown yielded releases of 15 kkg to air and 2 kkg to water as a result of benzene evaporation. It was estimated that releases to landfills or to solid residues due to export of benzene would be negligible.

6.0 NONCONSUMPTIVE USES OF BENZENE

Nonconsumptive uses are those in which benzene is not removed from the materials balance by chemical destruction or export. Examples are given and discussed below.

6.1 TOTAL NONCONSUMPTIVE USE

Nonconsumptive use is a minor category of benzene use. An economic input/output analysis for benzene (Neufeld et al. 1978) estimated that the categories of miscellaneous chemical conversions, solvent uses, and inventory changes accounted for only 5.1 percent of production in 1977. In the absence of independent data, the 5.1 percent factor was applied to 1978 data:

$$\begin{pmatrix}\text{Benzene}\\ \text{Consumed}\\ 1978\end{pmatrix}\begin{pmatrix}\text{Fraction of}\\ \text{Nonconsumptive}\\ \text{Use}\end{pmatrix} = \begin{matrix}\text{Benzene to}\\ \text{Nonconsumptive}\\ \text{Use}\end{matrix}$$

$$(5.23 \times 10^6 \text{ kkg}) \qquad (0.051) \qquad = \qquad 2.7 \times 10^5 \text{ kkg}$$

Assuming that the 1977 percentage factor is applicable, this value represents an upper bound for nonconsumptive uses, since it also contains an unknown amount of miscellaneous consumptive uses.

6.2 CATEGORIES OF USE

The categories of nonconsumptive uses for benzene are shown in Table 6.1. The amounts for each category are estimates and are discussed in the respective sections.

6.3 RELEASES BY CATEGORY OF USE

6.3.1 Use of Benzene as a Solvent

A small fraction of benzene production is used as a solvent in various processes. According to Neufeld et al. (1978), benzene use as a solvent has been dropping since the 1977 OSHA Emergency Benzene Standard and the issuance of a regulation by the Consumer Product Safety Commission banning benzene in consumer products. This conclusion was based on interviews with 405 companies that used benzene as a solvent in either chemical manufacturing processes or in consumer goods.

6.3.1.1 Locations of Use

Analysis of benzene sales for solvent use in 1976 revealed the following geographical distribution (Neufeld et al. 1978):

Table 6.1 Nonconsumptive Uses of Benzene

Use	Amount, 1978 (kkg)
Solvent (industrial)	9,500[1] 27,000[2]
Solvent (consumer products)	130
Inventory change	-272,000
Pesticide ingredient	Not available
Total	270,000[3]

1. Neufeld et al. (1978)
2. Mara and Lee (1978)
3. Maximum value, estimated independently in section 6.1; not the sum of uses.

Region	States	Benzene Solvent Use (% of Total)
West South Central	TX, LA, AR, OK	51
Middle Atlantic	NY, PA, NJ	31
East North Central	WI, IL, IN, MI, OH	10
East South Central	KY, TN, MS, AL	5
West North Central	ND, SD, NE, KS, MN, IA, MO	1

6.3.1.2 Amounts of Use

Two estimates of the amount of benzene used as a solvent are presented in Table 6.1. The 9,500 kkg value was estimated by Neufeld et al. (1978) by summing projections of 1978 usage. The projections were made after interviews with a substantial number of industry representatives. However, these projections were complicated by the OSHA and CPSC actions of 1977, and the uncertainty of the estimate is approximately +10%, -50%.

The second estimate (Mara and Lee 1978) was based on judgments of the fraction of total benzene production that is used nonconsumptively. Their estimate of 27,000 kkg used as solvents has an estimated uncertainty of ±80%.

Of the two estimates, the value of Neufeld et al. (1978) appeared to be more soundly based on industry data, and it is used in this report.

Complementing this estimate of solvent use in industrial processes was a study for the Consumer Product Safety Commission that identified sources of benzene in solvents used by consumers (Hillman et al. 1978). These authors accounted for an estimated 130 kkg of benzene present in hydrocarbon solvents. Calculation of this value is shown in Appendix C.

6.3.1.3 Releases Due to Solvent Use

Neufeld et al. (1978) reported on use of benzene as a solvent and the releases associated with this use. They estimated that benzene solvent was either released or destroyed by emission control processes. The fraction released was estimated from information on control systems obtained during interviews with representatives of companies using benzene as a solvent. JRB estimated releases due to benzene in consumer products by using data from Hillman et al. (1978). It was assumed that all of this benzene was released to air except benzene in the "home fuels" category, which was destroyed. These estimates are summarized in Table 6.2. These authors also documented the effect of the 1977 OSHA and CPSC actions on benzene use: estimated losses of benzene due to solvent use were 6,000 to 7,000 kkg in 1976 and only 2,900 kkg in 1978. Cyclohexane is replacing benzene in many solvent uses.

On the average, 50 percent of releases from benzene use as solvent were estimated to be airborne and 50 percent, waterborne. This estimate was based on the observations that chemical manufacturing, due to the

Table 6.2 Estimated Releases of Benzene Due to Use as a Solvent, 1978 (Sources: Neufeld et al. 1978; Hillman et al. 1978)

Solvent Use	Amount Used (kkg)	Amount Destroyed (kkg)	Releases (kkg)
General organic synthesis	7,400	6,400	1,000
Pharmaceutical synthesis	730	510	220
Small volume chemicals			
Aluminum alkyls	1,000	0	1,000
Alcohols	330	150	180
Paint removers	0	0	500[1]
Consumer products	130[2]	20	110
Total	9,600	7,100	3,000

1. Due to product manufactured before May 1977 and sold in 1978.
2. Estimate applies to 1977. Calculations supporting this estimate are shown in Appendix C-4.

nature of the synthesis processes, is more likely to cause releases to water, and that formulation uses are more likely to yield uncontrolled evaporation. With this estimated distribution, of the 3,000 kkg released because of solvent use in 1978, 1,500 kkg went to air and 1,500 kkg to water.

Releases of benzene due to disposal of solid residues were not quantifiable, but were estimated to be small. In order to evaluate these releases, it would be necessary to know the rate of production of benzene-containing residues, the percentage of benzene (by weight) in the residues, and the method of residue disposal.

Benzene may be carried over into products during use as a solvent in chemical synthesis. Although no quantitative information was sought, it was estimated by analogy to the major synthetic uses of benzene (Chapter 5) that this carry-over would be negligible.

6.3.2 Changes in Benzene Inventory

Changes in the inventory of benzene during a given year may be considered "negative" or "positive" nonconsumptive use. Releases from inventory have been considered under storage releases. The purpose of the present estimate of inventory change is to aid in balancing supplies with uses.

Benzene inventories on December 31, 1977, totaled 6.43 x 10^5 kkg (National Petroleum Refiners Association, as cited in Neufeld et al. 1978). The corresponding value for 1978 was 3.71 x 10^5 kkg (National Petroleum Refiners Association, personal communication, 1979). These values give an inventory drop of 2.72 x 10^5 kkg in 1978. The uncertainty for the decrease is ±50%, because of the possibility of incomplete reporting of industry to the trade association. This inventory drop is listed in the materials balance as a source of benzene.

6.3.3 Use as a Pesticide Ingredient

The EPA Pesticide Product Information File lists seven products containing benzene. The percentage of benzene in each product is also given, but the amount of each product formulated per year was not available, so total benzene used for this purpose could not be quantitated. Telephone interviews with the respective manufacturers might produce information on sales volume. Table 6.3 lists pesticide products containing benzene.

Table 6.3 Pesticide Products Using Benzene as an Active Ingredient

Product Registration No.	Label Data	Manufacturer
00299-00002	Martin's Formula No. 62 Screw Worm Smear for Horses and Mules. Type 50: Insecticides and Miticides. Form 53: Coating for Animals and Humans. 35% benzene.	C.J. Martin Co.
00327 - 00026	Dr. Rogers' Screw Worm Formula No. 62. Type 50, Form 53. 35% benzene.	Texas Phenothiazine Co.
00576 - 00008	Barry's Derma-Seal Screw Worm Killer. Type 50, Form 53. 53% benzene.	Suwannee Drug Co.
00728 - 00104	Texas Star Screw Worm Killer. Type 50, Form 53. 47.5% benzene.	Southland Pierson
00891 - 00094	Hercules Delmar Insecticide Toxicant. Type 50, Type 77: unclassified. 3% benzene.	Hercules Agricultural
03286 - 08076	Staffel's Screw Worm Compound, U.S. Formula M62. Type 50, Form 53. 34.71% benzene.	Staffel Co.
11556 - 00044	KRS for Horses. Type 50. 29.57% benzene.	Bayvet

7.0 USE OF BENZENE AS A FUEL COMPONENT

7.1 BENZENE IN GASOLINE

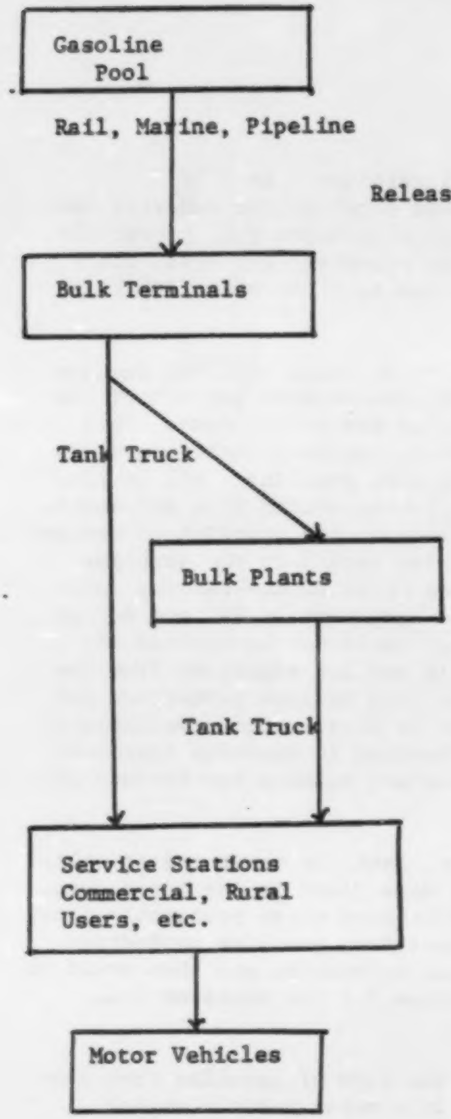
7.1.1 Overview

Benzene is an important constituent of gasoline. In 1978, 1.13623×10^{11} gallons of motor gasoline were supplied for domestic use (U.S. Department of Energy 1979). This figure includes U.S. production, releases from inventories, and imports, less exports. For 1978, the total amount of benzene in gasoline was estimated to be 4.4×10^6 kkg (see Section 7.1.2).

Benzene is present at low concentrations in crude oil (see Section 3.3). In the catalytic reformation process, the benzene content of the crude is increased when longer-chain molecules are broken down. This reformate, containing the aromatics (including benzene), makes up about 20 percent of the "pool" of materials going into gasoline. BTX (a mixture of benzene, toluene, and xylene) is often separated from reformate. Should an even higher concentration of benzene in the gasoline be desired to raise its octane rating, BTX may be blended back into the gasoline pool (USITC 1979). Thus, if benzene is used as an octane-raising additive, it is added to the gasoline pool as a component of BTX and not as pure benzene. In this situation the benzene would not be counted in reports of total benzene production since it was not separated from the BTX. Therefore, gasoline production, apart from benzene production per se, significantly contributes to the amount of benzene made available to the environment. A materials balance for benzene in gasoline therefore may be considered independently from a materials balance for benzene in general.

No factors for benzene releases to air, land, or water specifically attributable to the production of gasoline were found in the literature. Since gasoline is produced at petroleum refineries where presumably other processes are also taking place, any releases from gasoline production would be included in releases from petroleum refineries and thus would be beyond the scope of this chapter. See Section 3.1 for releases from petroleum refineries in general.

Figure 7.1 is a diagram representing the flow of gasoline from production center to its ultimate combustion in a motor vehicle engine. The distribution system, which transports gasoline from the petroleum refineries to the consumer with intermediate storage stops, is a significant source of atmospheric benzene. Gasoline is shipped from refinery storage areas to bulk terminals (regional distribution centers) by ship, barge, railcar, and pipeline. It is then transported from the terminal by tank truck to service stations and commercial and rural users, either directly or via bulk plants (local distribution centers)(Burklin et al. 1975; PEDCo 1977; Mara and Lee 1978). Benzene releases to air associated with particular segments of this flow are indicated in Figure 7.1, along with cross-references to the text. This chapter will follow the scheme presented in the flow diagram.


Gasoline Pool
Rail, Marine, Pipeline
Bulk Terminals
Tank Truck
Bulk Plants
Tank Truck
Service Stations Commercial, Rural Users, etc.
Motor Vehicles

	Section
Total gasoline produced: 1.14 x 10^{11} gal	7.1.1
Benzene Content: 1.17% lv	7.1.2
Releases: Transit to Terminal	7.1.3
Terminal Storage 3,570 - 5,730 kkg	7.1.4
Transit to Bulk Plants - Service Stations, etc.	7.1.5
Bulk Plant storage 1,190 - 1,360 kkg	7.1.6
Transit: Bulk Plant - Customer	7.1.7
Service Stations, etc. operations 1,210 - 6,550 kkg	7.1.8
Motor Vehicles Use	7.1.9
Total for Distribution and Use of Gasoline	7.1.10

Fig. 7.1 Gasoline Product Flow and Releases of Benzene to Air (adapted from Burklin et al. 1975)

For clarity, the subchapters on releases are divided into two parts. The first part consists of a description of release sources. The second part contains the data on benzene releases. The second part is divided into two sections, the first listing all the facts and factors used in calculating the releases of benzene related to that subchapter and the second part showing the actual calculations and their results. Wherever possible, for conciseness, common elements of the equations have been grouped together and evaluated separately.

It was not possible to evaluate independently the uncertainties of the numbers derived in this chapter because of the diverse sources of data entering into the estimates.

7.1.2 Content of Benzene in Gasoline

The benzene concentration in gasoline depends on several factors including the source of the crude oil from which the gasoline was made, the location of the crude oil source and the refiner, the grade of gasoline, refinery operations, and the seasonal blends produced by each refinery (PEDCo 1977).

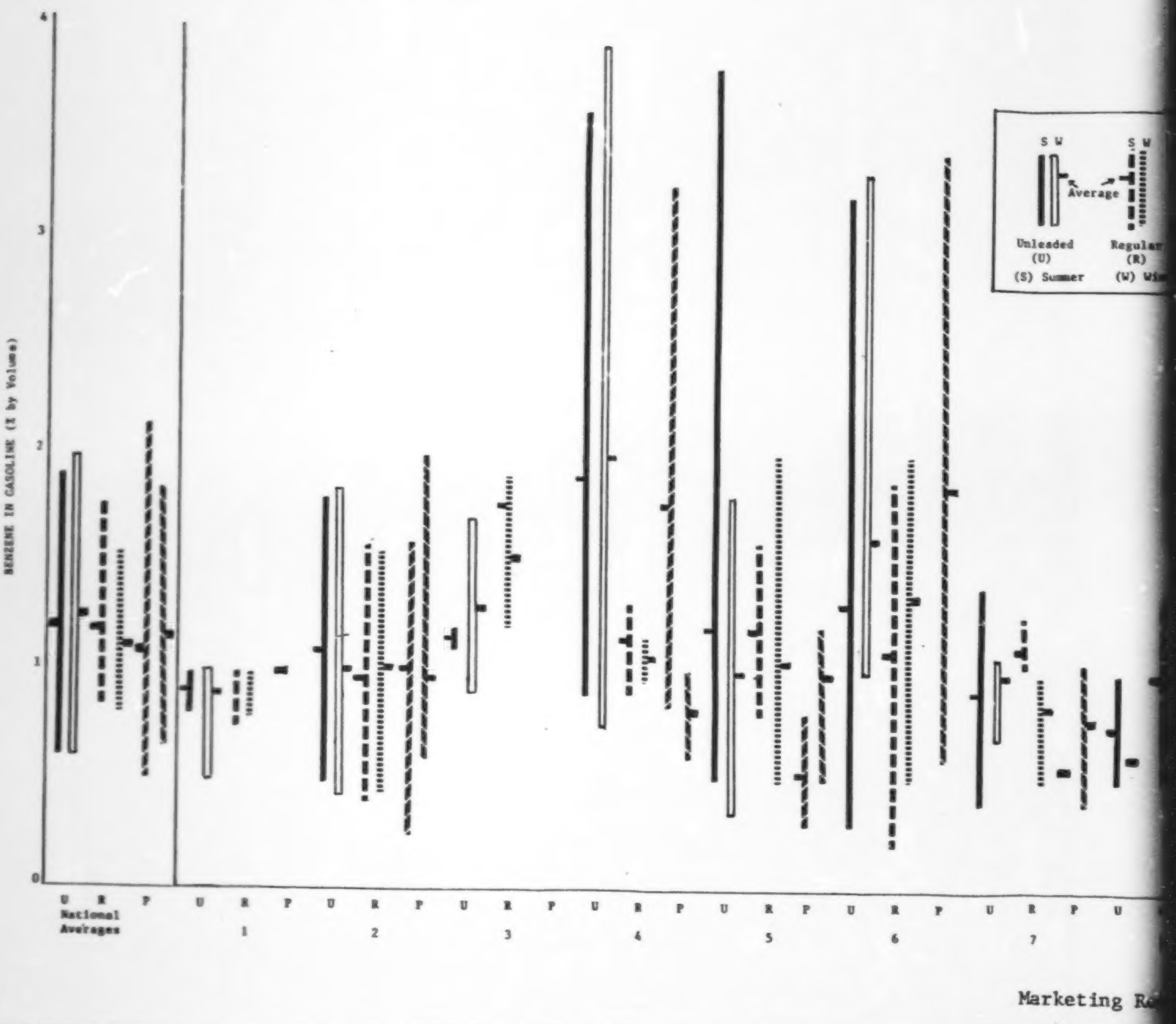
Prior to 1974, the average benzene content in U.S. gasoline was less than 1 percent by volume. More recent data indicate that the average benzene content has been increased to maintain octane levels as lead content has been reduced (Mara and Lee 1978). In a NIOSH study using 1976 data, the average benzene concentration was reported as 1.24 percent by volume; this was a weighted average taking into account different fuel types and amounts produced. A nationwide survey during February and March of 1977 produced a range of benzene concentrations from 1.25 to 5.0 percent by volume, averaging 2.5 percent.

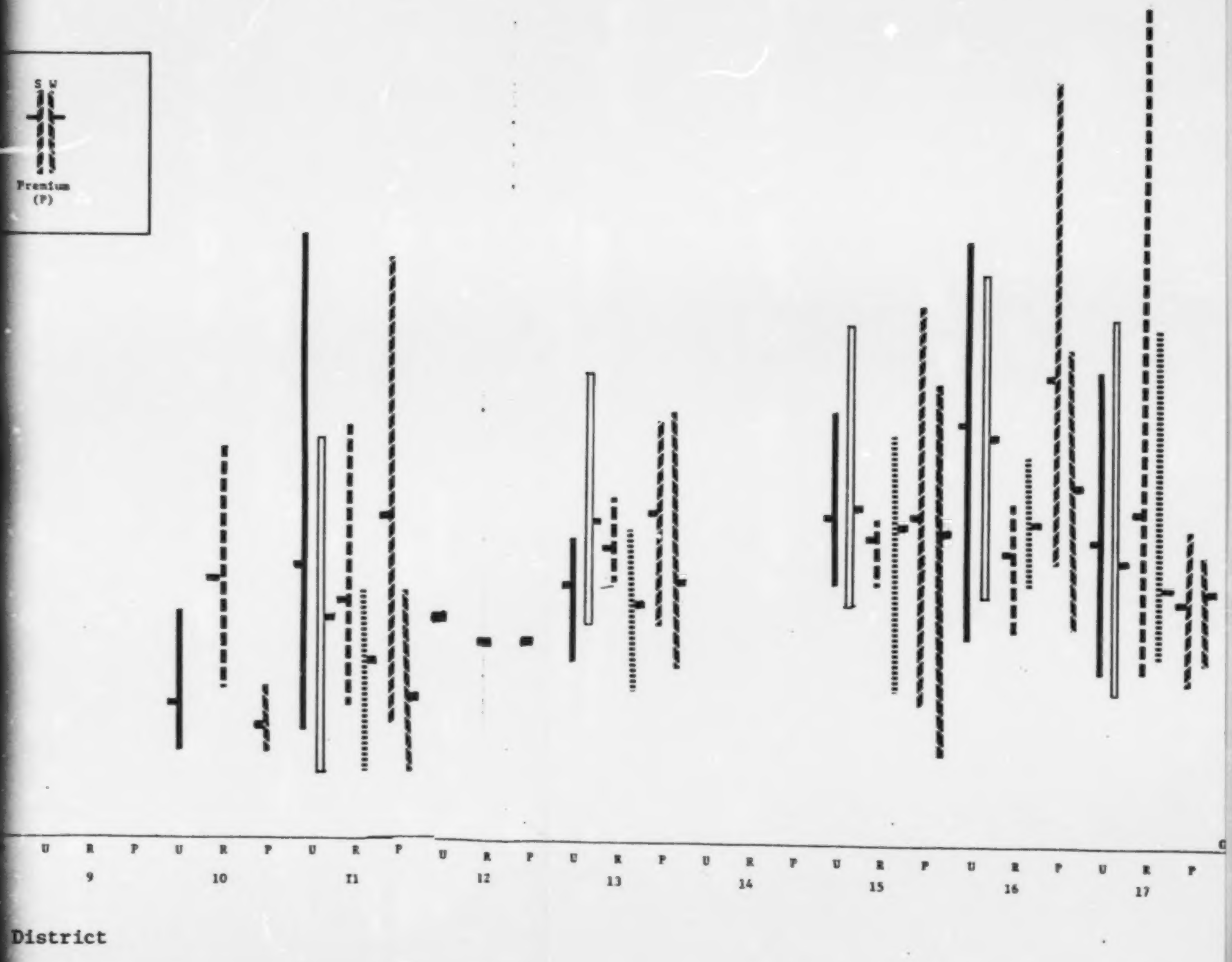
The most recent data on benzene in gasoline come from U.S. Department of Energy reports on motor gasoline for summer 1978 and winter 1978-1979 (Shelton 1979a, 1979b). Unleaded, regular, and premium grades of gasoline from various parts of the country were sampled during these two periods and tested for various properties including benzene content. These data are presented in diagrammatic form in Figure 7.2.

Figure 7.2 illustrates that the benzene content in gasoline is highly variable. From these data, one can find no significant differences regarding benzene content as a function of fuel grade or season. No correlation between average benzene content and marketing region is evident in these data; the variations within each region are actually much greater than the differences in averages from region to region.

The great variations are probably due to the nature of the gasoline refining and blending processes and the purpose for which gasoline is used. A wide range of compositions may fulfill the basic requirements for gasoline use. It has been reported that even raffinate is blended into gasoline (Getty 1980). Manufacturers are very concerned with octane ratings and must meet certain standards set by the federal government. Although benzene is an octane booster, there are other materials that may be so used. As was mentioned above, there appears to be no correlation between benzene content and fuel grade (higher octane premium actually averages slightly less benzene than regular).

Figure 7.2 Benzene in Gasoline





S W
Premium
(P)
U R P U R P U R P U R P U R P U R P U R P U R P U R P
9
10
11
12
13
14
15
16
17
District

The lowest reported benzene concentration in the surveys referred to above was 0.25 percent by volume (premium, summer, district 2). The highest benzene level was 0.91 percent (unleaded, winter, district 4). National averages from the reports (in percent by volume) were as follows:

	Unleaded	Regular	Premium
Summer	1.20	1.19	1.10
Winter	1.26	1.12	1.15

Since the differences in benzene concentrations between fuels of different grades and seasonal blends were smaller than the variation within each blend or grade, we have chosen the average of the above values, 1.17 percent, to represent benzene concentration in all gasolines for calculating releases and total amount of benzene in gasoline. In 1978, the total amount of benzene in gasoline was therefore:

$$\begin{array}{cccc} \begin{pmatrix}\text{Gasoline}\\ \text{Supply}\\ 1978\end{pmatrix} & \begin{pmatrix}\text{Percent}\\ \text{Benzene}\end{pmatrix} & & \begin{pmatrix}\text{Benzene in}\\ \text{Gasoline}\\ 1978\end{pmatrix} \\ (1.14 \times 10^{11}\text{ gal}) & (1.17) & = & 1.13 \times 10^{9}\text{ gal} \\ & & & 4.44 \times 10^{6}\text{ kkg} \end{array}$$

7.1.3 Benzene Releases Due to Transportation of Gasoline from Refinery to Bulk Terminal

7.1.3.1 Sources of Releases

As can be seen from Figure 7.1, gasoline leaves refinery storage by pipeline, marine barge, or rail tank car (Burklin et al. 1975). In 1967, U.S. bulk terminals reported receiving 42 percent of bulk liquid products by barge, and 35 percent by pipeline (Burklin et al. 1975). We assumed that the same percentages apply to gasoline in 1978, and that the balance (23 percent) was transported by rail tank car. (Release factors for tank cars and trucks are the same.) Since pipeline transportation is essentially a closed system from refinery to terminal, we assumed that there were no releases from pipeline transport.

Most releases during this phase of gasoline distribution resulted from loading operations. Loading losses occurred as hydrocarbon vapors present in the transport vehicle's cargo tank were displaced by the liquid being introduced. The vapor originated from the previous cargo that was carried and from the new cargo.

For tank cars there are two primary methods of loading: splash and submerged fill. With the splash method, the fill pipe dispensing the cargo is only partially lowered into the cargo tank; this results in a "free fall" of liquid through the vapor present in the tank. This results in significant liquid-vapor contact and turbulence, increasing the amount of liquid being evaporated. Liquid droplets may become entrained in the venting vapors and be carried out of the tank, resulting in a higher release level than with submerged loading (EPA 1977).

When the submerged fill method is used, the fill pipe is extended down into the liquid present in the cargo tank, and the cargo is introduced below the liquid surface. Liquid-vapor contact, and thus evaporation, is reduced, resulting in lower releases than with splash loading (EPA 1977).

Bottom loading is a type of submerged loading (with the same release characteristics). The cargo enters the tank from the bottom of the tank rather than the top (EPA 1977).

In transit, losses result from small quantities of hydrocarbon vapors being expelled from cargo tanks because of temperature and barometric pressure changes.

7.1.3.2 Amount of Releases

7.1.3.2.1 Assumptions, Facts, and Factors Used

1. (Assumption) Of all gasoline supplied for domestic use [1.14×10^{11} gallons in 1978 (U.S. Department of Energy 1979)], 35 percent was transported by pipeline; 42 percent was transported by marine conveyance (Burklin et al. 1975); and 23 percent was transported by rail car to bulk terminals (difference between above and 100 percent).

2. (Assumption) Gasoline has an average benzene content of 1.17 percent by volume (see Section 7.1.2).

3. (Factor) Assume that the vapor phase benzene concentration is 40 percent of the liquid concentration (45 percent on a vapor weight basis). That is, the ratio of benzene concentrations in vapor phase (percent by weight) to liquid phase (percent by volume) is 0.45 (PEDCo 1977).

4. (Factors) Release factors (from EPA publication AP-42 (1977) unless otherwise indicated):

Release Source	Uncontrolled Hydrocarbon Release Factor (lb/1,000 gallons transferred)
Loading:	
Tank car	
"Splash" method	12.4
"Submerged" method	4.10
Marine	2.88
Transit (all modes)	3/week (PEDCo 1977)
Unloading	
Tank car	2.10
Marine	2.52

5. (Assumption) Transit time (rail or marine) from refinery to bulk terminal is one week.

6. (Assumption) Releases are uncontrolled.

7.1.3.2.2 Calculations

$$\text{Factor } [A] = (1.14 \times 10^{11}\text{ gal supply})(1.17\ \%\ (v/v)\text{ benzene in gasoline})\left(0.45\ \frac{\%\ (w/w)\text{ in vapor}}{\%\ (v/v)\text{ in liquid}}\right) \times (454 \times 10^{-6}\text{ kkg/lb}) = 2.72 \times 10^{5}\ \frac{(\text{gal})\ (\text{kkg})\text{ benzene}}{\text{lb}}$$

Note: This factor has no physical significance by itself.

	Benzene Releases (kkg)
Pipeline transport: 35% of total gasoline supply.	
Closed system — no releases	0
Marine transport: 42% of total gasoline supply	
Loading: (42%) (2.88 lb/10^3 gal HC release factor) $\boxed{A}$ =	330
Transit: (42%)(3 lb/wk/10^3 gal HC release factor)(1 wk transit time) $\boxed{A}$ =	340
Unloading: (42%)(2.52 lb/10^3 gal HC release factor) $\boxed{A}$ =	290
Rail tank car: 23% of total gasoline supply	
Loading - splash method: (23%)(12.4 lb/10^3 gal HC release factor) $\boxed{A}$= Loading - submerged method: (23%)(4.10 lb/10^3 gal HC release factor) $\boxed{A}$=	260 - 780 (range)
Transit: (23%)(3 lb/wk/10^3 gal HC release factor)(1 wk transit time) $\boxed{A}$ =	190
Unloading: (23%)(2.10 lb/10^3 gal HC release factor) $\boxed{A}$ =	130
Total benzene releases due to transport of gasoline from refinery to bulk terminal =	1,500 - 2,100

7.1.4 Benzene Releases Due to Storage of Gasoline at Bulk Terminals

7.1.4.1 Sources of Releases

At terminals, gasoline may be stored in either floating-roof or fixed-roof tanks (Burklin et al. 1975), each with its own release characteristics. Although it is not known how many terminals have floating roofs, it is estimated that 70 to 80 percent do (Mara and Lee 1978). For the purposes of this report, we will assume that 75 percent of the gasoline supply is stored in floating-roof tanks, 25 percent in fixed-roof tanks.

Floating-roof tanks consist of a cylindrical shell equipped with a roof that floats freely on the stored liquid. The purpose of the floating roof is to reduce evaporative storage losses by minimizing vapor spaces. The roof rises and falls as the depth of the stored liquid changes. The roof is equipped with a sliding seal that fits against the tank wall, ensuring that the liquid surface is completely covered (EPA 1977).

Releases from floating tanks are of two types: standing storage and withdrawal. Standing storage losses result from an improper fit of the seal and shoe to the vessel shell, which exposes liquid surface to the atmosphere. A small amount of vapor may escape between the flexible membrane seal and the roof. Withdrawal losses result from evaporation of the stored liquid from the walls of the shell as the roof descends during emptying operations (EPA 1977).

Fixed-roof tanks, usually the least expensive to construct, consist of a cylindrical shell topped by a coned roof. They are generally equipped with a pressure/vacuum vent designed to contain minor vapor volume changes (EPA 1977).

Releases from fixed-roof tanks are of two types: breathing and working. Breathing losses consist of vapor expelled due to expansion caused by temperature and barometric pressure changes. Working losses are the result of filling and emptying operations. Filling loss is the result of vapor displacement by the incoming liquid. Emptying loss is the expulsion of vapors subsequent to product withdrawal, and is attributable to vapor increase as the newly inhaled air becomes saturated with hydrocarbons (EPA 1977).

According to A.D. Little, Inc. (1977), total bulk storage capacity at bulk terminals in 1976 was 735 million barrels; capacity was projected to be 1285 million barrels in 1980. We will use for 1978 the average, 1010 million barrels, or 4.24×10^{10} gallons. This capacity was distributed among 1,992 terminals.

7.1.4.2 Amount of Releases

7.1.4.2.1 Assumptions, Facts and Factors Used

1. (Fact) Total gasoline supplied for domestic use = 1.14×10^{11} gal in 1978 (U.S. Department of Energy 1979)

2. (Assumption) Gasoline has an average benzene content of 1.17% by liquid volume (see Section 7.1.2)

3. (Factor) The vapor phase benzene conversion is

$$0.45 \frac{\text{\% (w/w) benzene in vapor}}{\text{\% (v/v) benzene in liquid}} \quad \text{(PEDCo 1977)}$$

4. (Assumption) Of the total gasoline supply,
75% was stored in floating roof tanks, and
25% was stored in fixed-roof tanks (see text)

5. (Factors) Release factors: (from U.S. EPA (1977) publication AP-42 unless otherwise indicated)

Release Source	Uncontrolled Hydrocarbon Release Factor
Floating roof tank -	
standing storage - new tank	0.033 lb/day/10^3 gal capacity
- old tank	0.088 lb/day/10^3 gal capacity
(Burklin et al. 1975)	
withdrawal	0.025 lb/10^3 gal throughput
(PEDCo 1977)	
Fixed-roof tanks -	
breathing - new tank	0.22 lb/day/10^3 gal capacity
- old tank	0.25 lb/day/10^3 gal capacity
(Burklin et al. 1975)	
working	9 lb/10^3 gal throughput
(EPA 1977)	

6. (Assumption) Total U.S. storage capacity at bulk terminals =
4.24 x 10^{10} gal (see text)
25% = fixed roof tank capacity
75% = floating roof tanks capacity
(see text)

} assume supply is proportional to capacity

7. (Assumption) All releases are uncontrolled.

7.1.4.2.2 Calculation

$$\text{Factor } [B] = (1.17\%\ (v/v)\ \text{benzene in gasoline}) \times \left(0.45\ \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\right) \times (454 \times 10^{-6}\ \text{kkg/lb}) = 2.39 \times 10^{-6}\ \text{kkg benzene/lb}$$

(Note: This factor has no physical significance by itself.)

	Benzene Releases, (kkg)
Floating-roof tank: **Standing storage - new tanks:** (4.24×10^{10} gal storage capacity at terminals) (75% in floating roofs)(0.033 lb/day/10^3 gal capacity, HC release factor)(365 days/yr) x [B] = 920 **Standing storage - old tanks:** (4.24×10^{10} gal storage capacity at terminals) (75% in floating roofs)(0.088 lb/day/10^3 gal capacity, HC release factor)(365 days/yr) x [B] = 2,440 kkg	920-2,400 (range)
Withdrawal: (1.14 x 10^{11} gal gasoline supply) (75% in floating roof tanks)(0.025 lb/10^3 gal throughput, HC release factor) x [B] =	5.1
Fixed-roof tanks: **Breathing losses - new tanks:** (4.24×10^{10} gal storage capacity at terminals) (25% in fixed-roof tanks)(0.22 lb/day/10^3 gal capacity, HC release factor)(365 days/yr) x [B] = 2,000 kkg **Breathing losses - old tanks:** (4.24×10^{10} gal storage capacity at terminals) (25% fixed-roof tanks)(0.25 lb/day/10^3 gal capacity, HC release factor)(365 days/yr) x [B] = 2,300 kkg	2,000-2,300 (range)
Working losses: (1.14×10^{11} gal gasoline supply) (25% in fixed-roof tanks)(9 lb/10^3 gal throughput, HC release factor) [B] =	600
Total benzene releases due to storage of gasoline at bulk terminals =	3,500-5,300

7.1.5 Releases Due to Transportation of Gasoline from Bulk Terminals to Service Stations or Bulk Plants

7.1.5.1 Sources of Releases

In 1967, 80 percent of the bulk plants received their gasoline supplies from tank trucks (Burklin et al. 1975). Only a fraction of the total gasoline supply passes through bulk plants (see Section 7.1.6). We believe that all service stations receive their supplies from tank trucks. Release factors for trucks and rail tank cars are the same. Therefore, the amount of gasoline leaving bulk terminals by a transit mode other than truck or rail is very slight. We will assume for this section that all gasoline travels from bulk terminal to customer by tank truck.

The sources of releases from tank trucks are the same as those of rail tank cars. For a discussion of release sources for rail tank cars, refer to Section 7.1.3.1.

7.1.5.2 Amount of Releases

7.1.5.2.1 Assumptions, Facts and Factors Used

1. (Fact) Total gasoline supplied for domestic use = 1.14×10^{11} gal in 1978 (U.S. Department of Energy 1979).

2. (Assumption) Gasoline has an average benzene content of 1.17 percent by liquid volume (see Section 7.1.2).

3. (Factor) The vapor phase conversion factor, ratio

$$\frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} = 0.45 \text{ (PEDCo 1977)}$$

4. (Factor) Release factors (from EPA (1977) publication AP-42 unless otherwise indicated)

Release Source	Uncontrolled Hydrocarbon Release Factor
Truck loading	
splash method	12.4 lb/10^3 gal transferred
submerged method	4.10 lb/10^3 gal transferred
Transit	3 lb/wk/10^3 gal (PEDCo 1977)
Unloading	2.10 lb/10^3 gal transferred

5. (Assumption) Average transit time from bulk terminal to customer (service station or bulk plant) = 1 week

6. (Assumption) Releases are uncontrolled.

7.1.5.2.2 Calculations

$$\text{Factor [A]} = (1.14 \times 10^{11} \text{ gal supply})(1.17\% \text{ (v/v) benzene in gasoline})\left(0.45\ \frac{\%\text{ (w/w) benzene in vapor}}{\%\text{ (v/v) benzene in liquid}}\right) \times (454 \times 10^{-6} \text{ kkg/lb}) = 2.72 \times 10^{5} \text{ (gal benzene)(kkg/lb)}$$

(Note: This factor has no physical significance by itself.)

	Benzene Releases (kkg)
Truck transit:	
Loading - splash method: (12.4 lb/10^3 gal, HC release factor) [A] =	1,100 - 3,400 (range)
Loading - submerged method: (4.10 lb/10^3 gal, HC release factor) [A] =	
Transit: (3 lb/wk/10^3 gal, HC release factor) (1 wk transit time) [A] =	820
Unloading: (2.10 lb/10^3 gal HC release factor) x [A] =	572
Total benzene releases due to transport of gasoline from bulk terminal to service stations or bulk plants =	2,500 - 4,800

7.1.6 Benzene Releases Due to Gasoline Storage at Bulk Plants

According to A.D. Little, Inc. (1977) there were 21,116 bulk plants with a total storage capacity of 57 million barrels in the United States in 1976. The authors projected that if recent trends continue, there would be only 19,083 bulk plants with a storage capacity of 52 million barrels in 1980. Based on these estimates, we used the average, 55 x 10^6 barrels or 2.3 x 10^9 gallons capacity as a 1978 estimate. Bulk plants contain only 4 to 7 percent of the total U.S. petroleum storage capacity, but make 36 to 37 percent of the gasoline sales (by volume) (A.D. Little, Inc. 1977). We used the 36 percent estimate as representative of 1978. Based on this number and on the U.S. Department of Energy's value of 1.14 x 10^{11} gallons for the total 1978 gasoline supply, we estimated that 4.1 x 10^{10} gallons were handled by bulk plants.

7.1.6.1 Sources of Releases

Bulk plant storage facilities consist of above-ground and underground tanks. In a survey prepared for EPA, 65 percent of tanks were reported to be above ground, 30 percent were underground, and 5 percent were a combination of both (Shedd and Efird 1977). For the purposes of this report, we used the values of 67.5 percent above ground and 32.5

percent underground. Because storage tanks found at bulk plants are relatively small, the use of floating-roof tanks is not common (Shedd and Efird 1977). We assumed for this report that the above-ground storage at bulk plants consists entirely of fixed-roof tanks. For a discussion of sources of releases from fixed-roof tanks, see Section 7.1.4.1.

A discussion of sources of releases from underground gasoline storage is presented in Section 7.1.8.1.

7.1.6.2 Amount of Releases

7.1.6.2.1 Assumptions, Facts and Factors Used

1. (Assumption) Gasoline supply handled by bulk plants = 4.1×10^{10} gal (see text)

2. (Assumption) Storage capacity at bulk plants = 2.29×10^{9} gal

   67.5% in fixed-roof tanks
   32.5% in underground storage tanks } Assume supply is proportionate to capacity

3. (Assumption) Gasoline has an average benzene content of 1.17% by liquid volume (see Section 7.1.2)

4. (Factor) The vapor phase benzene conversion factor,

   $$\text{ratio } \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} = 0.45 \text{ (PEDCo 1977)}$$

5. (Factors) Release factors: (from EPA publication AP-42 (1977) unless otherwise indicated).

Release Source	Uncontrolled Hydrocarbon Release Factor
Fixed-Roof Tanks:	
Breathing - new tanks:	0.22 lb/day/10^3 gal capacity
- old tanks:	0.25 lb/day/10^3 gal capacity (Burklin et al. 1975)
Working	9 lb/10^3 gal throughput
Underground Storage:	
Splash loading	11.5 lb/1000 gal transferred
Submerged loading	7.3 lb/1000 gal transferred
Breathing	1 lb/1000 gal throughput (Burklin et al. 1975)
Unloading	1 lb/1000 gal transferred

6. (Assumption) Releases are uncontrolled.

7.1.6.2.2 Calculations

Factor [B] = (1.17% benzene in gasoline) x

$$0.45\ \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\ (454 \times 10^{-6}\ \text{kkg/lb}) =$$

2.39×10^{-6} kkg benzene/lb

(Note: This factor has no physical significance by itself.)

Benzene Releases, (kkg)

Releases from:

Fixed-roof Tanks:

Breathing - new tanks:

(2.29×10^9 gal storage capacity at bulk plants) (67.5% in fixed-roof tanks) (0.22 lb/day/10^3 gal capacity, HC release factor) (365 days/yr) [B] = 300

Breathing losses - old tanks:

(2.29×10^9 storage capacity at bulk plants) (67.5% in fixed-roof tanks) (0.25 lb/day/10^3 gal capacity, HC release factor) (365 days/yr) [B] = 340

300-340 (range)

Working losses:

(4.1×10^{10} gal gasoline supply handled by bulk plants) (67.5% in fixed roof tanks) (9 lb/10^3 gal throughput, HC release factor) [B] = 600

Underground Tanks:

Splash loading:

(4.1×10^{10} gal gasoline supply handled by bulk plants) (32.5% in underground tanks)(11.5 lb/10^3 gal transferred, HC release factor) [B] = 370

Submerged loading:

(4.1×10^{10} gal gasoline supply handled by bulk plants) (32.5% in underground tanks)(7.3 lb/10^3 gal transferred, HC release factor) [B] = 230

230-370 (range)

Breathing:

(4.1×10^{10} gal gasoline supply handled by bulk plants) (32.5% in underground tanks)(1 lb/10^3 gal throughput, HC release factor) [B] = 30

	Benzene Releases (kkg)
Unloading: (Same calculation as breathing) =	30
Total benzene releases due to storage at bulk plants =	1,200-1,400

7.1.7 Benzene Releases Due to Transportation of Gasoline from Bulk Plants to Service Stations and Other Customers

7.1.7.1 Sources of Releases

Gasoline is hauled to service stations and other customers of bulk plants by tank trucks. The sources of releases from the tank trucks are the same as those from rail tank cars. These releases are discussed in Section 7.1.3.1.

7.1.7.2 Amounts of Releases

7.1.7.2.1 Assumptions, Facts, and Factors Used

1. (Assumption) Total gasoline handled by bulk plants = 4.1×10^{10} gal (see Section 7.1.6.1).

2. (Assumption) Gasoline has an average benzene content of 1.17% (v/v) (see Section 7.1.2).

3. (Factor) The vapor phase benzene conversion ratio factor,

$$\frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} = 0.45$$

4. (Factors) Release factors: (from EPA publication AP-42 (1977) unless otherwise indicated)

Release Source	Uncontrolled Hydrocarbon Release Factor
Truck Loading:	
Splash method	12.4 lb/10^3 gal transferred
Submerged method	4.10 lb/10^3 gal transferred
Transit	3 lb/wk/10^3 gal (PEDCo 1977)
Unloading	2.10 lb/10^3 gal transferred

5. (Assumption) Average transit time from bulk plant to customer (service station, commercial-rural user, etc.) = 1 day

6. (Assumption) Releases are uncontrolled.

7.1.7.2.2 Calculations

Factor [B] = (1.17% (v/v) benzene in gasoline) x

$$0.45 \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} \ (454 \times 10^{-6}\ \text{kkg/lb}) =$$

2.39×10^{-6} kkg benzene/lb

(Note: This factor has no physical significance by itself.)

	Benzene Releases, (kkg)
Releases from truck transit:	
Loading - Splash method: (4.1 x 10^{10} gal amount gasoline handled by bulk plants) (12.4 lb/10^3 gal, HC release factor) [B] = 1,200 kkg	400- 1,200 (range)
Loading - Submerged method: (4.1 x 10^{10} gal amount gasoline handled by bulk plants) (4.10 lb/10^3 gal, HC release factor) [B] = 400 kkg	
Transit: (4.1 x 10^{10} gal amount gasoline handled by bulk plants) (3 lb/wk/10^3 gal HC release factor) (1 wk transit time) [B] =	41
Unloading: (4.1 x 10^{10} gal amount handled by bulk plants) (2.10 lb/10^3 gal, HC release factor) [B] =	200
Total benzene releases due to transport of gasoline from bulk plant to customer	600- 1,400

7.1.8 Benzene Releases Due to Service Station and Other Similar Operations

In 1973, 70 percent of the U.S. gasoline consumption was sold to passenger cars at 212,000 service stations. The remaining 30 percent was sold to industrial, commericial, rural customers or passenger cars at outlets other than service stations (Burklin et al. 1975). For the purpose of calculating releases and performing a materials balance, we assumed that the entire gasoline supply passed through a dispensing system similar to service stations, with the same release characteristics.

7.1.8.1 Sources of Releases

There are two principal sources of releases at service stations: underground tanks and refueling vehicle tanks (EPA 1977).

The filling of underground tanks causes releases through the displacement of resident hydrocarbon vapor by the incoming liquid gasoline. Underground storage tanks are filled by both the splash and submerged fill methods much as tank cars are filled (Section 7.1.3.1) (EPA 1977).

It has been reported that underground tanks, like other fixed volume tanks, breathe due to temperature and barometric pressure changes (Burklin et al. 1975), although the effect of temperature change is probably minimized by the tank's underground location.

Unloading of underground tanks is also listed as a source of releases at the rate of 1 lb/10^3 gal transferred (EPA 1977). Although no explanation of this release was presented, it seems reasonable. A release during unloading would probably occur when fresh air is drawn into the tank as the liquid level drops. As this air becomes saturated with hydrocarbon vapors, the volume of gas will expand causing a release to the atmosphere.

Vehicle refueling also is a source of releases. These releases are attributable to vapors displaced from the automobile tank by dispensed gasoline. Spillage also is a source of release. All gasoline spilled was assumed to evaporate; thus, no vapor phase conversion was necessary when determining benzene levels.

7.1.8.2 Amount of Releases

7.1.8.2.1 Assumptions, Facts, and Factors Used

1. (Fact) Total gasoline supplied for domestic use = 1.14 x 10^{11} gal in 1978 (U.S. Department of Energy 1979).
2. (Assumption) Gasoline has an average benzene content of 1.17% by volume (see Section 7.1.2).
3. (Factor) The vapor phase conversion factor

$$\frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} = 0.45\ \text{(PEDCo 1977)}$$

4. (Factors) Release factors: (from U.S. EPA publication AP-42 (1977) unless otherwise indicated).

	Hydrocarbon Release Factor
Filling Underground Storage Tank:	
Splash method	11.5 lb/10^3 gal transferred
Submerged - uncontrolled	7.30 lb/10^3 gal transferred
Subermged loading - open system	0.8 lb/10^3 gal transferred
Submerged loading - closed system	0

(continued)

Release Source	Hydrocarbon Release Factor
Underground Tank Breathing:	1 lb/10^3 gal throughput (Burklin et al. 1975)
Unloading:	1 lb/10^3 gal transferred
Vehicle Refueling Displacement Losses:	
Uncontrolled	9 lb/10^3 gal pumped
Controlled	0.9 lb/10^3 gal pumped
Spillage (all assumed to evaporate)	0.7 lb/10^3 gal

5. (Assumption) Uncontrolled releases are assumed unless otherwise indicated.

7.1.8.2.2 Calculations

Factor [A] = (1.14 x 10^{11} gal supply)(1.17% benzene in gasoline) x

$$\left(0.45 \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\right)(45 \times 10^{-6}\ \text{kkg/lb})$$

2.27 x 10^5 (gal benzene)(kkg)/lb

(Note: This factor has no physical significance by itself.)

		Benzene Releases, (kkg)
Releases from filling underground storage tanks:		
Splash method - (11.5 lb/10^3 gal transferred) [A] =	3,130 kkg	0-3,130 (range)
Submerged - uncontrolled - (7.30 lb/10^3 gal transferred) [A] =	1,990 kkg	
Submerged loading - open system - (0.8 lb/10^3 gal transferred, HC release factor) [A] =	200 kkg	
Submerged loading - closed =	0 kkg	
Releases from underground tank breathing:		
(1 lb/10^3 gal transferred, HC release factor) [A] =		300
Releases from unloading:		
(1 lb/10^3 gal transferred, HC release factor) [A]=		300

	Benzene Releases, (kkg)
Releases from vehicle refueling:	
Uncontrolled: (9 lb/10^3 gal HC release factor) [A] = 2,000	200-2,000 (range)
Controlled: (0.9 lb/10^3 gal HC release factor) [A] = 200	
Spillage (all assumed to evaporate):	
(0.7 lb/10^3 gal pumped, HC release factor) (1.14 x 10^{11} gal supply)(1.17% benzene in gasoline)(454 x 10^{-6} kkg/lb)=	400
Total benzene releases due to service station and similar operations	1,200-6,100

7.1.9 Vehicle Releases

In 1978, there were 153,919,922 motor vehicles registered with the states in the United States. These vehicles included 116,574,999 automobiles, 5,141,957 motorcycles, 500,362 buses, and 31,702,604 trucks (U.S. Department of Transportation 1978). This section will estimate benzene releases due to fuel combustion by these vehicles.

7.1.9.1 Source of Releases

Hydrocarbon releases from gasoline-powered vehicles without emission controls may be divided into two types: evaporative and exhaust releases. The evaporative releases originate from:

1. The carburetor (evaporation of fuel after a hot engine is turned off);
2. The fuel tank (from vents, with releases increasing as tank temperature increases);
3. The crankcase (from "blow-by" past the piston rings).

The exhaust releases result from incomplete combustion of the fuel (PEDCo 1977).

Benzene releases depend not only on benzene levels in gasoline, but also on particular characteristics of the gasoline blend. For example, if the fuel blend contains ethylbenzene, incomplete combustion may result in conversion of ethylbenzene to benzene; thus, more benzene might be exhausted than was present originally in the fuel (PEDCo 1977). In a materials balance, therefore, combustion of fuel in a vehicle engine should be considered both as a use and as a source of benzene. It would be difficult to determine how much exhaust benzene is attributable to noncombusted benzene originally present in the fuel, and how much is attributable to the breakdown of more complex substances.

Emission control systems in use on current-model motor vehicles include PCV (positive crankcase ventilation), EGR (exhaust gas recirculation), evaporative controls, and catalytic oxidation systems (PEDCo 1977).

7.1.9.2 Amounts of Releases from Automobiles

7.1.9.2.1 Assumptions, Facts, and Factors Used

1. (Fact) In 1978, there were 116,574,999 automobiles registered in the United States (U.S. Department of Transportation 1978).

2. (Fact) In 1978, the average passenger car was driven 10,046 miles (U.S. Department of Transportation 1978).

3. (Factors) Release factors: (from U.S. EPA publication AP-42 (1977) unless otherwise indicated)

   Evaporative:

   0.148 g benzene/trip
   3.3 trips/day (Mara and Lee 1978)

   or

   Using model year 1972 new car as a base

   1.76 g hydrocarbons/mile

   Exhaust: (EPA-ORD and General Motors estimate)(Gray 1979)

   0.005 - 0.020 g benzene/mile with catalytic converter
   0.005 - 0.15 g benzene/mile without catalytic converter

4. (Assumption) Estimate of vehicles with catalytic converters - lacking substantive data in this area, we used PEDCo's estimate (for 1976) of 73 percent with exhaust controls (PEDCo 1977).

5. (Assumption) For evaporative releases, assume the average benzene content in gasoline = 1.17 percent (v/v) (see Section 7.1.2).

6. (Factor) For evaporative releases, use a benzene vapor phase conversion factor of

$$0.45 \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}$$

7.1.9.2.2 Calculations of Releases from Automobiles

Benzene Releases, (kkg)

Evaporative: (method 1)

(116,574,999 automobiles)(3.3 trips/auto/day) x
(0.148 g benzene/trip) x (365 days/yr)
(1 x 10^{-6} kkg/g) = 21,000 kkg

(method 2)

(116,574,999 automobiles)(10,046 miles/auto) x
(1.76 g hydrocarbons/mile)(1.17% benzene gasoline) x

$$\left(0.45 \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\right) = 11{,}000\ \text{kkg}$$

11,000-
21,000
(range)

Exhaust: Automobiles with catalytic converters:

(73% vehicles with catalytic converter)(116,574,999 automobiles)(10,046 miles/auto)(0.005-0.020 g benzene/mile)(1 x 10^{-6} kkg/g) = 4,000 kkg - 17,000 kkg benzene released

4,000-
17,000
(range)

Automobiles without catalytic converters:

(27% vehicles without catalytic converters) x
(116,574,999 automobiles)(10,046 miles/auto) x
(0.05-0.15 g benzene/mile)(1 x 10^{-6} kkg/g) =
20,000 kkg-47,000 kkg benzene released

20,000-
47,000
(range)

Total automobile benzene releases:

Evaporative (methods 1 and 2)	11,000-21,000 kkg
Exhaust	24,000-64,000 kkg
Total:	35,000-85,000 kkg

35,000-
85,000

7.1.9.3 Amounts of Releases from Motorcycles

7.1.9.3.1 Assumptions, Facts, and Factors Used

1. (Fact) In 1978, there were 5,141,957 motorcycles registered in the United States (U.S. Department of Transportation 1978).
2. (Fact) In 1978, the average motorcycle traveled 4,500 miles (U.S. Department of Transportation 1978).
3. (Factors) Release factors: (from U.S. EPA (1977) publication AP-42 unless otherwise indicated)

Evaporative - 0.36 grams of hydrogen released per mile

Crankcase:

2 stroke engine - 0

4 stroke engine - 0.6

Exhaust:

2 stroke engine - 16

4 stroke engine - 2.9

4. For evaporative and crankcase releases:

   a) (Assumption) Average benzene concentration in gasoline = 1.17 percent (see Section 7.1.2).

   b) (Factor) The benzene vapor phase conversion factor,

$$\frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}} = 0.45$$

5. Conversion of exhaust hydrocarbon release factors to benzene release factors.

   Method: We are given an automobile hydrocarbon release factor for a model year 1972 new vehicle, of 3.02 g of hydrocarbons per mile (EPA 1977). We are also given a benzene release factor for vehicles of 0.05 to 0.1 g of benzene per mile (Gray 1979). From the ratio of these numbers, the benzene release factor is 1.7 to 5 percent of the hydrocarbon release factor.

   Applying these numbers to the exhaust release factors above results in:

   Exhaust benzene release factors:

   2 stroke engine - 0.27 - 0.8 g/mile

   4 stroke engine - 0.05 - 0.15 g/mile

7.1.9.3.2 Calculations of Benzene Releases from Motorcycles

	Benzene Releases, (kkg)
Evaporative:	
(5,141,957 motorcycles)(4,500 miles/motorcycle) x (0.36 x 10^{-6} kkg/mile hydrocarbon release factor)(1.17% benzene in gasoline) $\left(0.45\ \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\right)$ =	44

	Benzene Releases, (kkg)
Crankcase:	
4 stroke engine: (5,141,957 motorcycles)(4,500 miles/motorcycle) x (0.6 x 10^{-6} kkg/mile hydrocarbon release factor)(1.17% benzene in gasoline $\left(0.45\ \frac{\%\ (w/w)\ \text{benzene in vapor}}{\%\ (v/v)\ \text{benzene in liquid}}\right) =$ 73 kkg	0-73 (range)
2 stroke engines: 0 kkg	
Range of crankcase releases: 0-73 kkg	
Exhaust:	
2 stroke engine: (5,141,957 motorcycles)(4,500 miles/motorcycle) x ((0.05-0.15) x 10^{-6} kkg benzene/mile) = 1,000-3,000 kkg benzene	
Therefore, range of motorcycle exhaust benzene releases =	1,000-19,000
Total benzene releases from motorcycles =	1,000-19,000

7.1.9.4 Amounts of Releases from Trucks and Buses

7.1.9.4.1 Assumptions, Facts, and Factors Used

1. (Facts) Vehicle registrations and average number of miles driven per vehicle class (U.S. Department of Transportation 1978).

   a) Buses: 500,362 (12,143 miles/vehicle)

   b) Trucks: 31,702,604

      i) single unit - 30,336,022 (9,249 miles/vehicle)
      ii) combination - 1,366,582 (49,267 miles/vehilcle)

2a. (Assumption) The Department of Transportation (1978) reports that of commercial buses, 14,187 are gasoline-powered and 87,371 are powered by diesel and other fuels; i.e., 14 percent of the commercial buses on the road are gasoline-powered. Applying this percentage to all buses registered, we estimate that 70,000 buses are gasoline-powered.

b. (Assumption) Trucks: Lacking data in this area we assumed for the purposes of this report that all single unit trucks are gasoline-powered and fall into the AP-42 classification of light-duty trucks (EPA 1977). We also assumed that all combination trucks are powered by diesel and other fuels, and thus would fall beyond the scope of this subchapter.

3. (Assumption) We assumed that buses fall into the AP-42 emission category of heavy-duty gasoline-powered trucks (EPA 1977).

4. (Assumption) In choosing release factors for trucks and buses, we used the factors for new model year 1972 vehicles.

5. (Assumption) For evaporative emissions, we assumed a benzene content in gasoline of 1.17 percent (see Section 7.1.2) and a benzene vapor phase conversion factor of

$$0.45 \frac{\%\ (w/w) \text{ benzene in vapor}}{\%\ (v/v) \text{ benzene in liquid}} \quad \text{(PEDCo 1977).}$$

6. (Factors) Release factors (from U.S. EPA publication AP-42) (1977), model year 1972 new vehicles, hydrocarbon releases

Light duty trucks:

Evaporative:	3.1 g/mile
Exhaust:	3.4 g/mile

Heavy duty trucks (buses):

Evaporative:	5.8 g/mile
Exhaust:	13.6 g/mile

The literature contained no information on the benzene content of hydrocarbon exhaust releases from gasoline-powered motorcycles, light trucks, or heavy duty trucks/buses.

7. Conversion of exhaust hydrocarbon emission factors to exhaust benzene release factors (see Section 7.1.9.3.1, note 5).

7.1.9.4.2 Calculation of Benzene Releases from Trucks and Buses

	Benzene Releases, (kkg)
Light duty trucks:	
Evaporation:	
(30,336,022 trucks)(9,249 miles/truck) x (3.1 x 10^{-6} kkg/mile hydrocarbon release factor) x (1.17% benzene gasoline) x $\left(0.45 \frac{\%\ (w/w) \text{ benzene in vapor}}{\%\ (v/v) \text{ benzene in liquid}}\right) =$	4,600
Exhaust:	
(30,336,022 trucks)(9,249 miles/truck) x ((0.06 - 0.2) x 10^{-6} kkg benzene/mile) =	17,000- 56,000 (range)

	Benzene Releases, (kkg)
Heavy duty trucks (buses)	
Evaporation:	
(70,000 gasoline-powered buses)(12,143 miles/bus) x (5.8 x 10^{-6} kkg hydrocarbon release factor) x (1.17% benzene in gasoline)(0.45 vapor conversion factor) =	30
Exhaust:	
(70,000 gasoline-powered buses)(12,143 miles/bus) x ((0.2-0.7) x 10^{-6} kkg benzene/mile) =	200-600 (range)
Total benzene releases from gasoline-powered trucks and buses =	22,000-61,000 (range)

7.2 BENZENE CONTENT OF OTHER FUELS

The benzene concentrations of eight fuels were estimated by Arthur D. Little, Inc. (1977) and are presented in Table 7.1. The estimated benzene contents, calculated from these concentrations, are also presented. These calculations indicate that a significant quantity of benzene is present in aviation turbine fuel, which consists of naphtha and kerosene types of jet fuel. Because of the magnitude of this estimate, JRB recommends further investigation to determine the quantity of benzene released from this fuel.

No information was provided on the reliability of the data used in the calculations, nor were any independent criteria available which would have permitted the calculation of uncertainty ranges for these estimates.

Table 7.1 Estimated Benzene Content of Fuels

Benzene-Containing Fuels[1]	Fuel Produced in 1978[2] (gallons)	Estimated Benzene Concentration (% by Volume)	Benzene Produced as a Component of Fuel (kkg)
Aviation Gasolines	5.85×10^8	0.4 - 3[4]	38,000
Farm Tractor Fuels	?	0 - trace[5]	?
Diesel Fuel Oils	5.26×10^{10}	0 - trace[5]	200
Aviation Turbine Fuels	1.62×10^7	0 - 3[4]	921,000
Gas Turbine Fuel Oils	?	0 - trace[5]	?
Liquefied Petroleum Gases	1.5×10^7	0	0
Fuel Oils	4.63×10^7	0 - trace[5]	200
Kerosene	2.7×10^6	0 - trace[5]	10

1. Source: Arthur D. Little Inc. (1977).
2. U.S. Department of Energy 1979: The data were connected from barrels to gallons using the conversion factor of 42 gallons/barrel.
3. Jet fuel is the total of naphtha and kerosene types.
4. An arithmetic average was used in the calculation of benzene concentration.
5. Arthur D. Little (1977) gave no indication of what "trace" meant. We have assumed that trace is 1 part per million.

8.0 SUMMARY OF DISPOSAL/DESTRUCTION AS END-PRODUCTS

No data were collected that permitted evaluation of the disposal of benzene-containing residues or the destruction of benzene-containing end-products. It was judged, however, that benzene would readily volatilize from landfilled solid residues. The question of benzene reformation during destruction of end-products remains open.

9.0 LOCATIONS OF BENZENE RELEASE SITES

Table 9.1 summarizes the estimated benzene releases at each site containing at least one production or use facility. Releases were estimated for each plant individually by using its estimated production and a release factor applicable to the plant process. Estimated production and relevant release factor for use sites were taken directly from Chapter 5. For benzene production sites it was necessary to estimate benzene production at each refinery by each of the four production processes. To do this, estimated production figures from Table 2.2 were allocated equally among the processes used at each refinery. The applicable release factor for each process was calculated from the estimated releases in Table 2.13 by the operation:

$$\begin{array}{c}\text{Release Factor}\\ \text{for Catalytic}\\ \text{Reformation}\end{array} = \left(\begin{array}{c}\text{Releases due to}\\ \text{Catalytic}\\ \text{Reformation}\end{array}\right) \div \left(\begin{array}{c}\text{Estimated Produc-}\\ \text{tion by Catalytic}\\ \text{Reformation}\end{array}\right)$$

These release factors were judged to be order-of-magnitude estimates because of the substantial uncertainties in both the release estimates and the allocation of production among the processes used at a given plant. Releases for each plant site were calculated from the estimated production and appropriate release factor:

$$\begin{array}{c}\text{Release at Site A}\\ \text{Due to Catalytic}\\ \text{Reformation}\end{array} = \left(\begin{array}{c}\text{kkg Produced}\\ \text{by Catalytic}\\ \text{Reformation}\\ \text{at Site A}\end{array}\right)\left(\begin{array}{c}\text{Release Factor}\\ \text{for Catalytic}\\ \text{Reformation}\end{array}\right)$$

Releases by county or state venues were the sums of estimated releases by all benzene users and producers in the venue.

These counties and states are ranked in decreasing order of air releases in Table 9.1. The five areas with the greatest potential for exposure from air releases were estimated to be Iberville Parish (LA); Harris County (TX); Galveston County (TX); Midland, MI; and Puerto Rico.

Table 9.1 Geographic Locations of Benzene Release Sites

State	County	Estimated Releases To Air, kkg/yr
TX	all	5,735
	Harris	1,300
	Galveston	1,278
	Unknown	795
	Jefferson	729
	Nueces	706
	Brazoria	580
	Ector	155
	Howard	131
	Schleicher	50
	Cass	11
LA	all	1,990
	Iberville	1,410
	St. James	325
	Unknown	142
	Bossiev	48
	St. Charles	23
	Orleans	22
	Ascension	20
MI	all	975
PR	all	875
PA	all	859
MO	all	730
IL	all	658
NJ	all	621
WV	all	555
KY	all	295
MD	all	207
OH	all	198
CA	all	166

Table 9.1 Geographic Locations of Benzene Release Sites (Con't)

State	County	Estimated Releases To Air, kkg/yr
VI	all	140
MI	all	75
OK	all	70
VT	all	43
CO	all	32
KS	all	28
NY	all	26
AL	all	21

10.0 SUMMARY OF UNCERTAINTIES

Table 10.1 summarizes all significant values used in this report and the estimated range or precision for each. As used in the table, N.B. means No Basis for Evaluation.

Table 10.1 Summary of Uncertainties

Section	Description of Value	Value	Estimated Range or Precision
2.0	1978 direct benzene production from petroleum	4,780,000 kkg	± 2%
2.0	1978 direct benzene production from coal	178,000 kkg	± 2%
2.1.2, 2.1.3.1	Total 1975-1979 capacity for benzene production from petroleum	various	± 20%
2.1.2	1975-1979 capacity for benzene production from petroleum for a given plant	various	± 20%
2.1.2	Total 1975-1979 benzene production from petroleum	See Figure 2.1	± 10%
2.1.2	1975-1979 benzene production from petroleum for a given plant	See Figure 2.1	± 30%
2.1.3.1	Total 1978 capacity for benzene production from petroleum through catalytic reformation	3,500,000 kkg	± 20%
2.1.3.1	Total 1978 production of benzene from petroleum through catalytic reformation	2,360,000 kkg	± 30%
2.1.3.2	Maximum possible releases during extraction	2,360	+ 500%, -50%
2.1.3.2	Benzene release factor due to production through catalytic reformation	0.01 kkg/kkg	N.B.
2.1.3.2	Benzene releases due to production through catalytic reformation	20,000 kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.1.4.1	Total 1978 capacity for benzene production from petroleum through toluene dealkylation	1,920,000 kkg	± 20%
2.1.4.1	Total 1978 production of benzene from petroleum through toluene dealkylation	1,300,000 kkg	± 30%
2.1.4.2	Releases of benzene from the dealkylation method (1978)	1,300 kkg	+500%, -200%
2.1.5.1	Total 1978 capacity for benzene production from petroleum through toluene disproportionation	180,000 kkg	± 20%
2.1.5.1	Total 1978 production of benzene from petroleum through toluene disproportionation	121,000 kkg	± 30%
2.1.5.2	Releases of benzene due to transalkylation and disproportionation method	60 kkg	+50%, -70%
2.1.6.1	Total 1978 capacity for benzene production from petroleum from pyrolysis gasoline	1,320,000 kkg	± 20%
2.1.6.1	Total 1978 production of benzene from petroleum from pyrolysis gasoline	925,000 kkg	± 30%
2.1.6.2	Releases of benzene due to pyrolysis gasoline method	180 kkg	+300%, - 100%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.1.7	Benzene release factor to air due to benzene production from petroleum (all benzene production methods that use petroleum)	1.8×10^{-5} kkg/kkg (See Table 2.13)	low reliability
2.1.7	Benzene releases to air due to benzene production from petroleum (all benzene production methods that use petroleum)	86 kkg	low reliability
2.1.7	Benzene release factor to water due to benzene production from petroleum (all benzene methods that use petroleum)	1.3×10^{-4} kkg/kkg (See Table 2.13)	± a factor of 1,000
2.1.7	Benzene releases to water due to benzene production from petroleum (all benzene production methods that use petroleum)	620 kkg	± a factor of 1,000
2.1.8.1	Benzene release factors to air due to benzene storage	See Table 2.16	N.B.
2.1.8.1	Benzene releases to air due to benzene storage	105–4,900 kkg	N.B.
2.1.8.2	Benzene production that was not captively used	2,560,000 kkg	± 30%
2.1.8.2	Benzene release factors to air due to benzene loading	See Table 2.17	N.B.
2.1.8.2	Benzene releases to air due to benzene loading	various	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.1.8.3	Benzene release factors to air due to benzene transport	See Table 2.18	N.B.
2.1.8.3	Benzene releases to air due to transport	various	N.B.
2.1.8.4	Total benzene releases to air due to transportation, loading, and storage of benzene	2,400-7,200 kkg	N.B.
2.2.1	Total 1975-1979 capacity for benzene production from coal	See Figure 2.2	± 20%
2.2.1	1975-1979 capacity for benzene production from coal for a given plant	See Figure 2.2	± 20%
2.2.1	Total 1975-1979 benzene from coal	See Figure 2.2	± 10%
2.2.1	1975-1979 benzene production from coal for a given plant	See Figure 2.2	± 30%
3.1.	Benzene release factors to air due to indirect production of benzene from petroleum refineries	See Table 3.1	N.B.
3.1	Benzene releases to air due to indirect production of benzene from petroleum refineries operating at 1977 capacity	20,000 kkg	N.B.
3.1	Benzene release factor to water due to indirect production of benzene from petroleum refineries	$1.64 \times 10^{-10} \frac{\text{kkg}}{\text{bbl}}$	± a factor of 10

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
3.1	Total 1978 benzene releases to water due to indirect production of benzene from petroleum	1 kkg	± a factor of 10
3.1	1978 benzene releases by state to water due to indirect production of benzene from petroleum refineries	See Figure 3.1	± a factor of 10
3.1	Annual coal consumption capacity of coke producing plants	88,000,000 kkg	± 20%
3.2	Walker's (1976) benzene release factor to air due to coke oven operations	$9.80 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg coke produced}}$	± a factor of 6
3.2	Total benzene releases, based on Walker's (1976) emission factor, to air due to coke oven operations	59,200 kkg	± a factor of 6
3.2	PEDCo's (1977) benzene release factor to air due to coke oven operations	$7.8 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	± a factor of 10
3.2	Total benzene releases based on PEDCo's (1977) emission factor due to coke oven operations	6,600 kkg	± a factor of 10
3.2	Mara and Lee's (1978) benzene release factor to air due to coke oven operations	$3 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
3.2	Total benzene releases based on Mara and Lee's (1978) emission factor due to coke oven operations	3,000 kkg	N.B.
3.2	Benzene releases by state based on Mara and Lee's (1978) emission factor due to coke oven operations.	See Figure 3.2	N.B.
3.3	Annual oil discharge to oceans according to Walker (1976)	11-12 x 10^9 lbs/year	N.B.
3.3	Benzene content of oils	0.001 - 0.4%	± a factor of 400
3.3	Annual benzene discharge to oceans according to	10-11 x 10^3 kkg	± a factor of ≥400
3.3	Annual oil discharge to U.S. waters according to Versar (1977)	4,990,691 gal	N.B.
3.3	Annual benzene discharge to U.S. waters according to Versar (1977)	30 kkg	± a factor of ≥400
3.4	Gross annual discharge of benzene to water from various indirect sources	various	N.B.
4.1	1975-1979 benzene imports	See Table 4.1	± 20%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
4.2	Benzene release factor for marine loading during importation	$2.0 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg unloaded}}$	$\pm$ a factor of 10
4.2	Benzene release factor for transport of imported benzene	$1 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg transported/wk}}$	$\pm$ a factor of 10
4.2	Total 1978 benzene releases due to benzene	25 kkg	$\pm$ a factor of 10
4.2.1	1978 benzene releases to air due to benzene imports	13 kkg	$\pm$ a factor of 15
4.2.2	1978 benzene releases to water due to benzene imports	13 kkg	$\pm$ a factor of 15
5.1	Total 1978 consumptive use of benzene	5,389,000 kkg	$\pm$ 20%
5.2	1975-1979 consumption of benzene for derivative synthesis	See Table 5.2	$\pm$ 20%
5.2	1978 production of each benzene derivative	See Table 5.1	$\pm$ 10%
5	Capacities for production of each benzene derivative	various	$\pm$ 10%
5	Production of each benzene derivative by a given plant	various	$\pm$ 30%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5	Consumption of benzene for the synthesis of each benzene derivative (except anthraquinone and biphenyl) by a given plant	various	± 40%
5.3.8.2	Benzene consumption for anthraquinone synthesis	23,000 kkg	N.B.
5.3.9.3.	Benzene consumption for biphenyl synthesis	11,000 kkg	± 50%
5.3.1.3.1	Benzene release factors to air and corresponding 1978 emissions due to ethylbenzene synthesis	See Table 5.3	N.B
5.3.1.3.2	Benzene release factor to water due to ethylbenzene synthesis	1.9×10^{-4} kkg/kkg	± a factor of 5
5.3.1.3.2	1978 benzene releases to water due to ethylbenzene synthesis	720 kkg	± a factor of 10
5.3.2.3	Benzene release factor due to cumene synthesis	0.25×10^{-3} kkg/kkg	N.B.
5.3.2.3	1978 benzene releases to air due to cumene synthesis	380 kkg	N.B.
5.3.3.3	Benzene release factor due to cyclohexane synthesis	2.8×10^{-3} kkg/kkg	± a factor of 10
5.3.3.3.1	Benzene releases to air due to cyclohexane synthesis	3,000 kkg	± a factor of 10

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5.3.3.3.2	Benzene releases to water due to cyclohexane synthesis	30 kkg	± a factor of 10
5.3.4.3.1	Benzene release factor to air due to maleic anhydride synthesis	0.20 kkg/kkg	+10%, -90%
5.3.4.3.1	1978 benzene releases to air due to maleic anhydride synthesis	3,600 kkg	+30%, -70%
5.3.4.3.2	1978 benzene releases to water due to maleic anhydride synthesis	8 kkg	N.B.
5.3.5.3.1	Benzene release factors and corresponding 1978 benzene releases to air due to nitrobenzene synthesis	See Table 5.12	N.B.
5.3.6.2.1	Benzene release factors to air due to chlorobenzene synthesis	See Table 5.6	N.B.
5.3.6.2.1	1978, 1979 benzene releases to air due to chlorobenzenes synthesis	See Table 5.7	N.B.
5.3.7.2	Amount of benzene consumed in alkylbenzene synthesis	132,000 kkg	± 30%
5.3.7.3.1	Benzene release factor to air due to alkylbenzene synthesis	5×10^{-4} kkg/kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5.3.7.3.1	1978 benzene releases to air due to alkylbenzene synthesis	170 kkg	N.B.
5.3.9.3	Benzene release factor due to biphenyl synthesis	5.9×10^{-3} kkg benzene emitted per kkg benzene consumed	± a factor of 2
5.3.9.3.1	1978 benzene releases to air due to biphenyl synthesis	64 kkg	± a factor of 3
5.3.9.3.2	1978 benzene releases to water due to biphenyl synthesis	0.3 kkg	± a factor of 3
6.1	Total 1978 nonconsumptive use of benzene	270,000 kkg	+ 0%, - 60%
6.3.1.2	1978 solvent nonconsumptive use of benzene according to Neufeld et al. (1978)	9,500 kkg	+10%, -50%
6.3.1.2	1978 solvent nonconsumptive use of benzene according to Mara and Lee (1978)	27,000 kkg	± 80%
6.3.1.3	1978 benzene releases due to solvent nonconsumptive use of benzene	2,900 kkg	N.B.
6.3.1.3.1	1978 benzene releases to air due to solvent nonconsumptive use of benzene	1,500 kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
6.3.1.3.2	1978 benzene emissions to water due to solvent nonconsumptive use of benzene	1,500 kkg	N.B.
6.3.2.	Change of benzene inventory in 1978	272,000 kkg	± 50%
7.1.1	Volume percent benzene in gasoline	1.7% (v/v)	± 50%
7.1.2	1979 Annual Domestic Gasoline Consumption (ADGC)	1.11×10^{11} gal	± 10%
7.1.2.	Amount of benzene in gasoline, 1979	1.3×10^{9} gal; 4.4×10^{6} kkg	± 60%
7.1.3.2	Capacity of floating-roof storage tanks	2.3×10^{6} gal	N.B.
7.1.3.2	Average tank retention time	30 days	N.B.
7.1.3.2	Average percent of tank filled	75%	N.B.
7.1.3.2	Release factor for hydrocarbon standing storage losses	132 lb/day/tank	N.B.
7.1.3.2	Release factor for hydrocarbon withdrawal losses	0.025 lb/10^{3} gal	N.B.
7.1.3.2	Conversion factor, benzene liquid volume to benzene vapor weight	0.45	± 5%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.2	Releases of benzene to air during standing storage, 1979	1,000 kkg	N.B.
7.1.3.2	Releases of benzene to air during withdrawal, 1979	10 kkg	N.B.
7.1.3.2	Daily volume of gasoline handled by bulk plants	4,000 gal	± 25%
7.1.3.2	Number of bulk plants, 1979	20,000	± 20%
7.1.3.2	Annual volume of gasoline handled by bulk plants	3×10^{10} gal	± 50%
7.1.3.2	Releases of benzene to air due to tank breathing, 1979	500 kkg	N.B.
7.1.3.2	Percent above-ground fixed-roof tanks at bulk plants	70%	± 10%
7.1.3.2	Annual volume stored in above-ground fixed-roof tanks	2×10^{10} gal	± 60%
7.1.3.2	Releases of benzene to air from filling above-ground fixed-roof tanks	1,600 kkg	± a factor of 4
7.1.3.2	Releases of benzene from filling underground tanks	1,000 kkg	± a factor of 4

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.2	Releases of benzene due to all gasoline storage	4,000 kkg	minimum: does not consider all possible losses
7.1.3.3 through 7.2	All other values	various	N.B.

11.0 DATA GAPS AND RECOMMENDATIONS

In the course of performing this Level II materials balance, the following significant data gaps were encountered:

11.1 RELEASES DUE TO BENZENE PRODUCTION BY COKE OVEN PLANTS

Light oil containing benzene is produced as a byproduct of coal coking. In Section 3.2 of the Level I report, a question arose concerning the fate of 472,000 kkg of benzene-containing light oil produced by coke ovens. This amount was the difference between the light oil production capacities of non-benzene-producing plants (798,000 kkg) and the amount of light oil accounted for by sales to other plants for benzene extraction (326,000 kkg). The question was not addressed in this report, and a more detailed literature search and inquiries to the appropriate companies are needed to determine what fraction of this unaccounted-for light oil is a source of benzene releases.

This problem is one aspect of the larger question of benzene releases due to coal coking. The coal coking process is under study at Office of Air Quality Planning and Standards, and was not investigated in detail in the present report.

11.2 TREATMENT OF SOLID RESIDUES

Data on production and treatment of benzene-containing solid residues (tars, gums, sludges) were unavailable for the Level I study and only small amounts of information on this topic were accessed in this Level II study. Industry sources should be interviewed for information on both refinery solids and solid residues formed during consumptive use. Information on rates of solid generation, compositions of residues, and disposal methods and efficiencies should be sought.

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Huruch, Herbert; National Petroleum Refiners Association
Lantaff, Bill; Getty Refining and Marketing Co.
Looney, Jes; Cosden Oil & Chemical Co.
Mueller, Dav; Standard Oil Co. of California-Chevron Chemical Co.
Nelson, Jimmy; American Petroleum Institute
North, Jim; Coastal States Corp., Coastal States Petrochemical Co.
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Strauser, John; Gulf Oil Corp.
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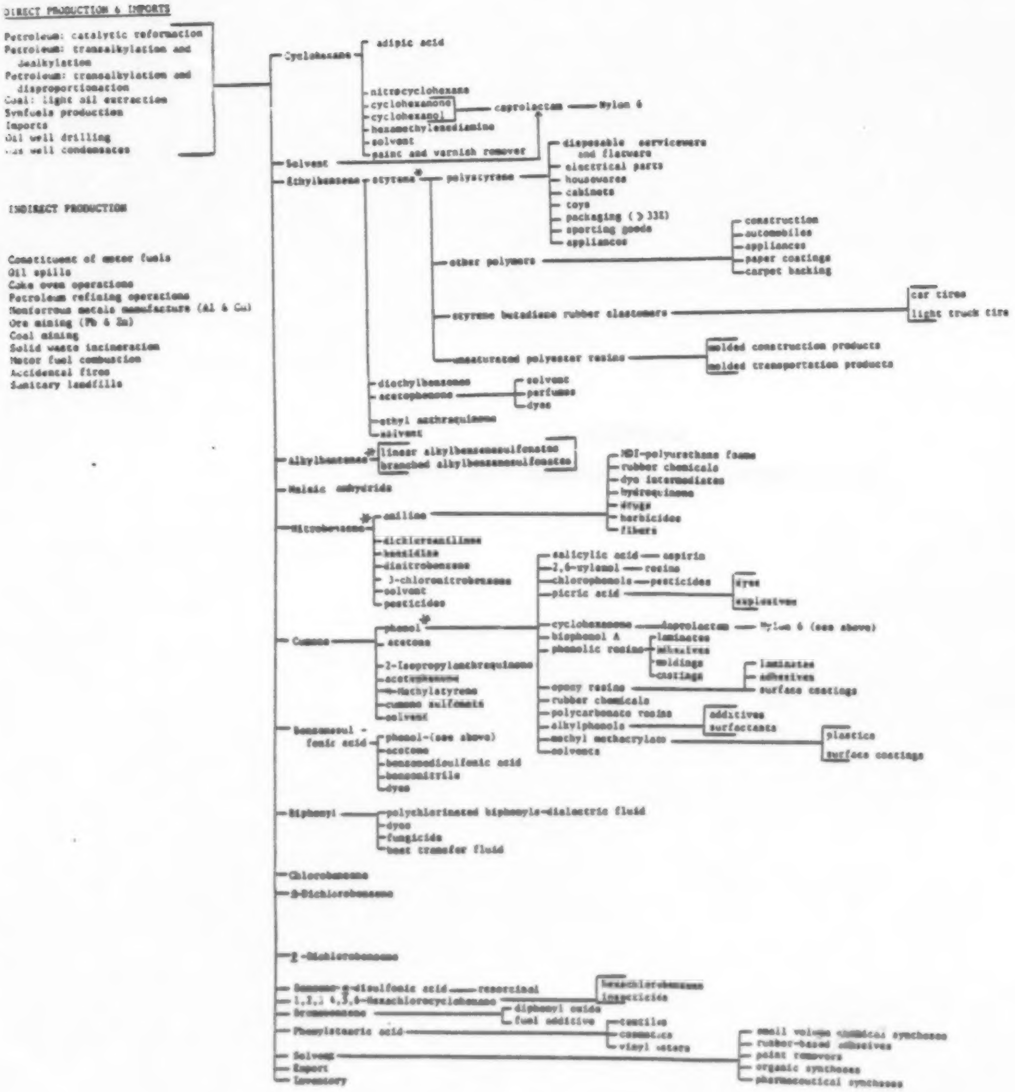
APPENDIX A

ENVIRONMENTAL FLOW DIAGRAM FOR BENZENE

Appendix A Environmental Flow Diagram for Benzene


DIRECT PRODUCTION & IMPORTS
Petroleum: catalytic reformation
Petroleum: transalkylation and dealkylation
Petroleum: transalkylation and disproportionation
Coal: light oil extraction
Synfuels production
Imports
Oil well drilling
Gas well condensates
INDIRECT PRODUCTION
Constituent of motor fuels
Oil spills
Coke oven operations
Petroleum refining operations
Nonferrous metals manufacture (Al & Cu)
Ore mining (Pb & Zn)
Coal mining
Solid waste incineration
Motor fuel combustion
Accidental fires
Sanitary landfills
Cyclohexane
adipic acid
nitrocyclohexane
cyclohexanone
cyclohexanol
caprolactam
Nylon 6
hexamethylenediamine
solvent
paint and varnish remover
Solvent
Ethylbenzene
styrene*
polystyrene
disposable serviceware and flatware
electrical parts
housewares
cabinets
toys
packaging (> 33%)
sporting goods
appliances
other polymers
construction
automobiles
appliances
paper coatings
carpet backing
styrene butadiene rubber elastomers
car tires
light truck tire
unsaturated polyester resins
molded construction products
molded transportation products
diethylbenzenes
acetophenone
solvent
perfumes
dyes
ethyl anthraquinone
solvent
Alkylbenzenes*
linear alkylbenzenesulfonates
branched alkylbenzenesulfonates
Maleic anhydride
Nitrobenzene*
aniline
MDI-polyurethane foams
rubber chemicals
dye intermediates
hydroquinone
drugs
herbicides
fibers
dichloroanilines
benzidine
dinitrobenzene
3-chloronitrobenzene
solvent
pesticides
Cumene
phenol*
salicylic acid — aspirin
2,6-xylenol — resins
chlorophenols — pesticides
picric acid
dyes
explosives
cyclohexanone — caprolactam — Nylon 6 (see above)
bisphenol A
phenolic resins
laminates
adhesives
moldings
coatings
epoxy resins
laminates
adhesives
surface coatings
rubber chemicals
polycarbonate resins
alkylphenols
additives
surfactants
methyl methacrylate
plastics
surface coatings
solvents
acetone
2-Isopropylanthraquinone
acetophenone
α-Methylstyrene
cumene sulfonate
solvent
Benzenesul-fonic acid
phenol-(see above)
acetone
benzenedisulfonic acid
benzonitrile
dyes
Biphenyl
polychlorinated biphenyls-dielectric fluid
dyes
fungicide
heat transfer fluid
Chlorobenzene
o-Dichlorobenzene
p-Dichlorobenzene
Benzene-m-disulfonic acid — resorcinol
1,2,3,4,5,6-Hexachlorocyclohexane
hexachlorobenzene
insecticide
Bromobenzene
diphenyl oxide
fuel additive
Phenylstearic acid
textiles
cosmetics
vinyl esters
Solvent
small volume chemical syntheses
rubber-based adhesives
paint removers
organic syntheses
pharmaceutical syntheses
Export
Inventory

* This compound and its products may yield benzene upon disposal

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APPENDIX B

PROCESS FLOW DIAGRAMS FOR PRODUCTION AND USES OF BENZENE

B-1 Refinery Flow Diagrams B-1

B-2 Sources of Benzene B-4

B-3 Aromatic Extraction Processes B-6

B-4 Catalytic Reformation B-11

B-5 Toluene Dealkylation B-19

B-6 Toluene Disproportionation B-20

B-7 Benzene from Pyrolysis Gasoline B-22

B-8 Coal Processing B-26

B-9 Ethylbenzene Production B-27

B-10 Cumene Production B-28

B-11 Cyclohexane Production B-29

B-12 Maleic Anhydride Production B-30

B-13 Nitrobenzene Production B-31

B-14 Chlorobenzenes Production B-32

B-15 Biphenyl Production B-33

Appendix B-1 Refinery Flow Diagrams

The following two figures represent flow diagrams of an integrated refinery coupled with a petrochemical complex. The catalytic reformate can either be used for gasoline production or used as feedstock in a petrochemical complex. Industrial contacts stated that due to economic considerations the aromatics are normally extracted from the catalytic reformate before it enters the gasoline pool.

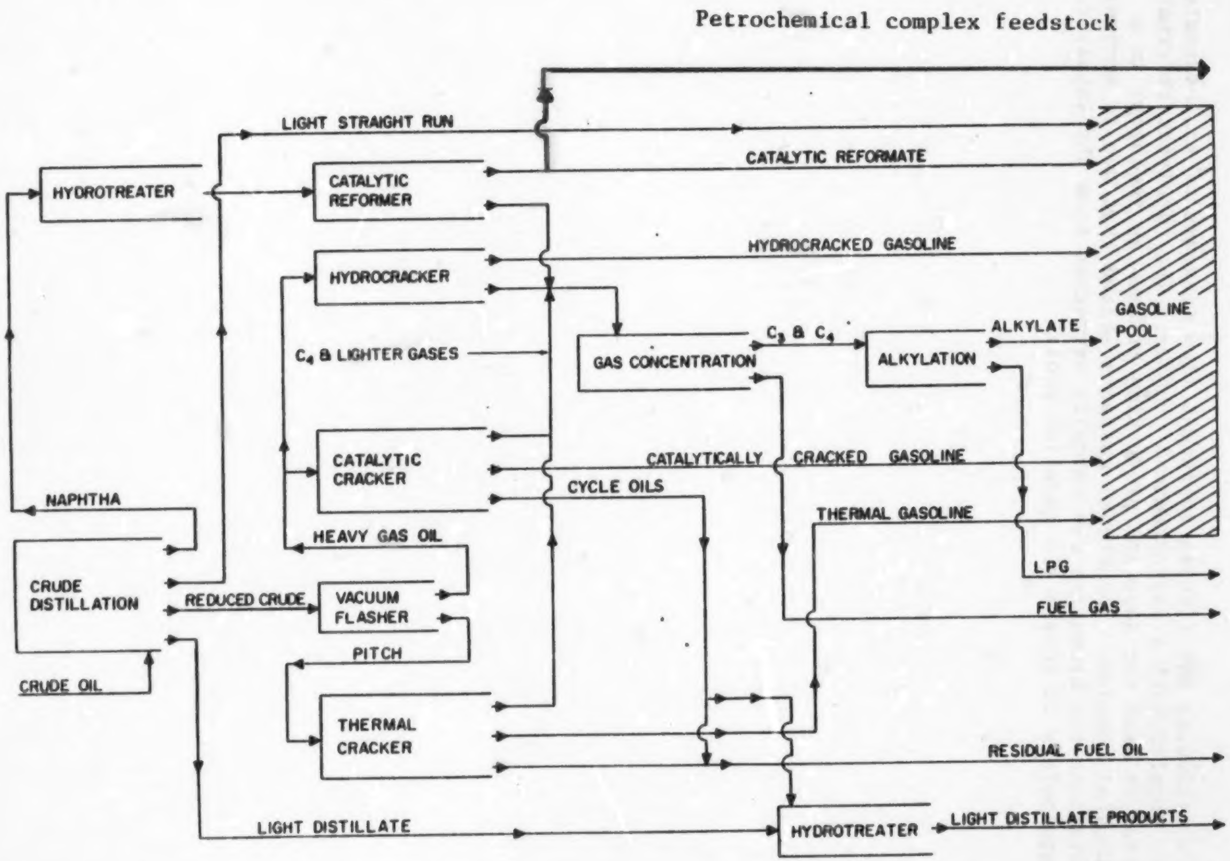

Petrochemical complex feedstock
LIGHT STRAIGHT RUN
HYDROTREATER
CATALYTIC REFORMER
CATALYTIC REFORMATE
HYDROCRACKER
HYDROCRACKED GASOLINE
GASOLINE POOL
C_3 & C_4
ALKYLATE
GAS CONCENTRATION
ALKYLATION
C_4 & LIGHTER GASES
CATALYTIC CRACKER
CATALYTICALLY CRACKED GASOLINE
CYCLE OILS
THERMAL GASOLINE
NAPHTHA
HEAVY GAS OIL
CRUDE DISTILLATION
REDUCED CRUDE
VACUUM FLASHER
LPG
FUEL GAS
PITCH
CRUDE OIL
THERMAL CRACKER
RESIDUAL FUEL OIL
LIGHT DISTILLATE
HYDROTREATER
LIGHT DISTILLATE PRODUCTS

Figure B-1. Process and Materials Flow Diagram for an Integrated Refinery for Manufacturing Fuels[1]

[1] Adapted from Considine 1974.

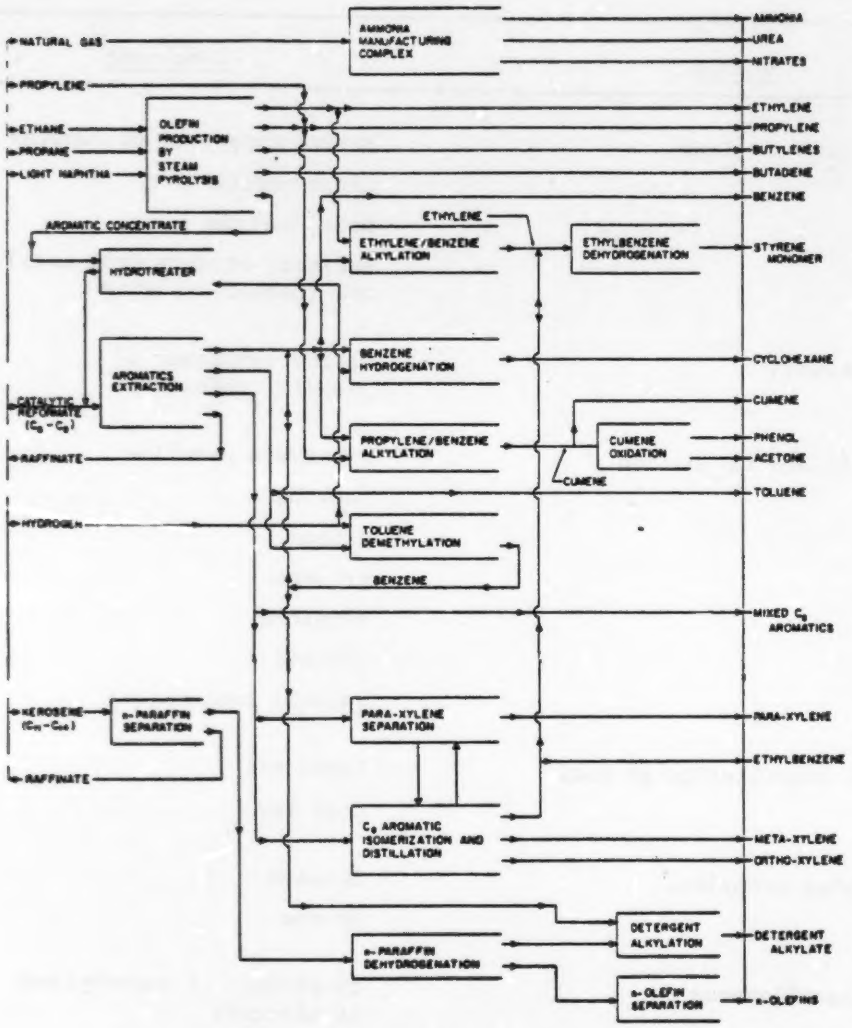

NATURAL GAS
AMMONIA MANUFACTURING COMPLEX
AMMONIA
UREA
NITRATES
PROPYLENE
ETHANE
PROPANE
LIGHT NAPHTHA
OLEFIN PRODUCTION BY STEAM PYROLYSIS
ETHYLENE
PROPYLENE
BUTYLENES
BUTADIENE
BENZENE
AROMATIC CONCENTRATE
ETHYLENE
ETHYLENE/BENZENE ALKYLATION
ETHYLBENZENE DEHYDROGENATION
STYRENE MONOMER
HYDROTREATER
AROMATICS EXTRACTION
CATALYTIC REFORMATE ($C_6 - C_9$)
BENZENE HYDROGENATION
CYCLOHEXANE
CUMENE
RAFFINATE
PROPYLENE/BENZENE ALKYLATION
CUMENE OXIDATION
PHENOL
ACETONE
CUMENE
TOLUENE
HYDROGEN
TOLUENE DEMETHYLATION
BENZENE
MIXED C_8 AROMATICS
KEROSENE ($C_{11} - C_{16}$)
n-PARAFFIN SEPARATION
PARA-XYLENE SEPARATION
PARA-XYLENE
ETHYLBENZENE
RAFFINATE
C_8 AROMATIC ISOMERIZATION AND DISTILLATION
META-XYLENE
ORTHO-XYLENE
DETERGENT ALKYLATION
DETERGENT ALKYLATE
n-PARAFFIN DEHYDROGENATION
n-OLEFIN SEPARATION
n-OLEFINS

Figure B-2. Process and Materials Flow Diagram for a Petrochemical Complex[1]

[1] Adapted from Considine 1974.

Appendix B-2 Sources of Benzene

Table B-1 List of Benzene Feedstocks

Source	Component
Crude petroleum	Native component of benzene
	Light naphtha cut
	Heavy naphtha cut
	Refinery streams from catalytic and thermal cracking
Gaswells	Native component of gaswell condensates
Ethylene production	Pyrolysis gasoline
	naphtha
	ethane
	propane
	n-butane
	gas oil
	gaswell condensates
By distillation of coal	Light oil
	Coal tar
Other aromatics	Toluene
	Xylene
Miscellaneous	By-product of naphthylene manufacture
	Straight chained unsaturated hydrocarbons in proper conditions
	Benzene precursors under proper conditions other than direct benzene production
	cyclohexane methyl-cyclohexane dimethyl-cyclohexane hexane methylcyclopentane

The above-mentioned sources were gleaned from several literature entries. All of the sources are of some economic value, except those listed under the miscellaneous heading. Some of the components under the ethylene production source are not of economic importance: ethane, propane and butane.

Table B-2. Aromatic Extraction Processes

Industrial Application	Aromatic Recovery Process	Process Description	Aromatic Feedstock Separation	Percent Aromatic Concentration Required for Process
Most frequently used method for the recovery of pure benzene and toluene. It is estimated that this method will increase in usage as greater quantities of heavy crudes are used to a greater extent.	Liquid-Liquid Extraction	The process is based on the selective aromatic extraction by a polar solvent in mixtures creating two immiscible components. This process generally is created in an extraction column. A. The extraction column process is as follows: 1. Solvent added at the head of the extractor. 2. Mixture to be separated is added at the middle. 3. Pure aromatics are reintroduced to the lower part of the column to create an "aromatic reflex" causing a distinct separation between the aromatic charged solvent and the nonaromatic fraction. 4. The aromatic charged solvent is emitted from the lower part of the extractor. 5. The nonaromatics are released from the upper end of the extractor.	Benzene, Toluene and Xylene (BTX) Components from "reformate gasoline."	Low aromatic content (20-65%)

Table B-2 (Continued)

Industrial Application	Aromatic Recovery Process	Process Description	Aromatic Feedstock Separation	Percent Aromatic Concentration Required for Process
		6. The aromatics may be separated from the solvent by: a. Directly distilled by steam stripping b. Extraction 1. Aromatics are disolved out of the extractor solvent by using a light hydrocarbon (pentane). 2. The aromatics are freed from the light hydrocarbon solvent by simple distillation. B. Refer to table for commercial process particulates.		
Second most frequently used process. Narrow cuts of Benzene and toluene from crude distillation. It is estimated that the usage of this method will decrease	Extractive distillation	The basic process mechanism is based on the properties of selective solvents to increase the boiling points between aromatics and nonaromatics. A. Extraction column separation process:	BTX components from pyrolysis gasoline	Medium aromatic content (65-90%)

Table B-2 (Continued)

Industrial Application	Aromatic Recovery Process	Process Description	Aromatic Feedstock Separation	Percent Aromatic Concentration Required for Process
due to the high purity required		1. Solvent and narrow cuts of benzene or toluene fraction are added to an extraction column.		
It is estimated that the usage of this method will decrease due to the high purity required.	Azeotropic distillation	The basic process mechanism is to use a solvent to increase the volatility of the nonaromatics. The extraction column separation process is stated below: A. A strongly polar auxiliary substance (i.e. acetone) is added to the benzene and nonaromatic mixture. B. The solvent increases the volatility of the nonaromatics which allows them to be extracted from the head of the extraction column. C. The benzene is extracted from the bottom of the extraction column.	BTX component from pyrolysis gasoline or light oil	High aromatic content (greater than 90%)
Rarely used today for the separation of benzene	Absorption on solids	The basic process mechanism is the selective separation of aromatic and nonaromatic mixtures by the use of high surface area solids	Benzene from coke-oven gas. It is estimated	It is estimated that the benzene needs to make up a high percentage

Table B-2 (Continued)

Industrial Application	Aromatic Recovery Process	Process Description	Aromatic Feedstock Separation	Percent Aromatic Concentration Required for Process
		having absorption specificity. Two common processes are stated below: A. Benzene is isolated from coke-oven gas using activated carbon. B. The Arosorb process is the separation of benzene and toluene from mixtures containing nonaromatics by adsorption with silica gel. 1. The nonaromatics are distilled off from the top of the extraction column, while the aromatics with the solvent are extracted from the bottom. 2. The solvent and benzene or toluene are separated by using a stripping column stream. Steam is frequently used as the stripping agent. 3. The stripped benzene is usually treated with	that a narrow cut of toluene/ benzene would be used in the second process.	of the mixture.

Table B-2 (Continued)

Industrial Application	Aromatic Recovery Process	Process Description	Aromatic Feedstock Separation	Percent Aromatic Concentration Required for Process
		Fullers earth to improve color and remove traces of unsaturated products. C. Types of solvents normally used are: 1. N-methylpyrrolidone (Distapex process) 2. N-formylmorpholine (Morphylane process) 3. Dimethylformamide 4. Sulfolane		
Only in special cases is this method used to separate benzene	Crystallization by freezing	The basic process mechanism is dependent on the separation of aromatics by their melting points.	Unknown	It is estimated that the benzene needs to make up a high percentage of the mixture.

(1) The information contained in the table was adopted from Industrial Organic Chemistry by Klaus Weissermel and Hans-Jurgen Arpe.

Appendix B-4 Catalytic Reformation

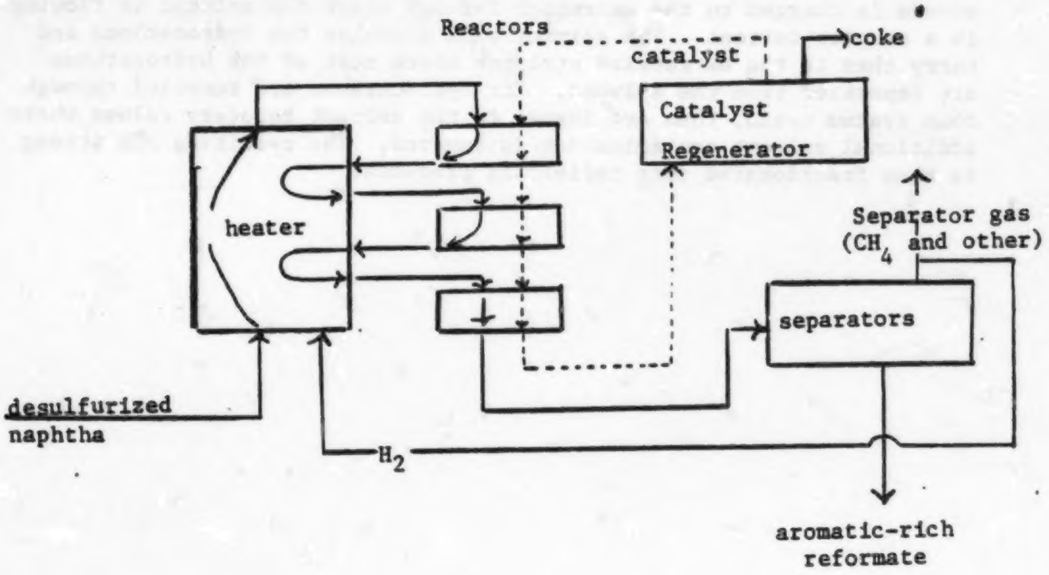

Reactors
catalyst
coke
Catalyst Regenerator
heater
Separator gas
(CH_4 and other)
separators
desulfurized naphtha
H_2
aromatic-rich reformate

Figure B-3 Platforming Method of Catalytic Reformation (Kirk-Othmer 1976)

Desulfurized naphtha is mixed with recycled hydrogen, heated, then fed through a series of moving catalyst bed reactors with intermediate heating. The platinum chloride-rhenium chloride catalyst is regenerated by controlled combustion coke removal, and is recycled. The reformate from the reactors passes through the separator where hydrogen and other gases are removed. The aromatic-rich reformate then goes to a stabilizer. Aromatics are extracted from the stabilized reformate.

Appendix B-4 (continued)

An example of the separation process is the Sulfolane process which is presented schematically on the next page. An aliphatic-aromatic stream is charged to the extractor through which the solvent is flowing in a counter-current. The solvent will dissolve the hydrocarbons and carry them to the extractive stripper where most of the hydrocarbons are separated from the solvent. The hydrocarbons are recycled through this system again, then are issued to the extract recovery column where additional solvent contamination is removed. The resulting BTX stream is then fractionated into individual products.

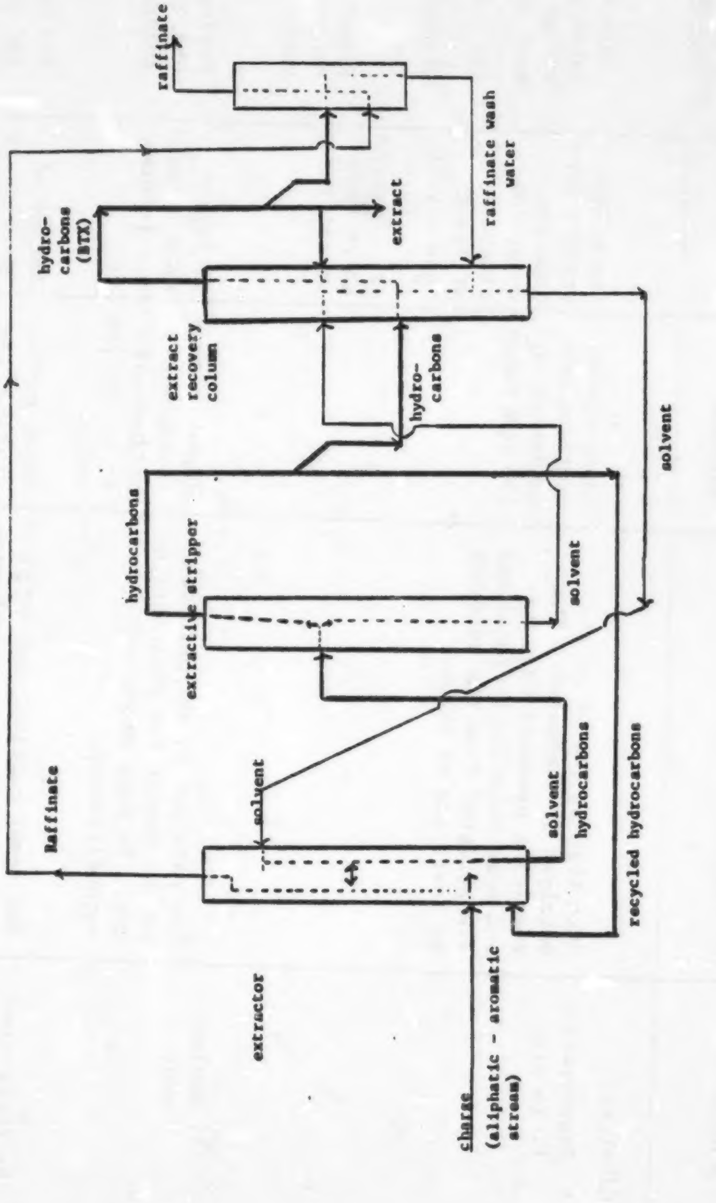

raffinate
raffinate wash water
extract
hydro-carbons (BTX)
extract recovery column
hydro-carbons
solvent
hydrocarbons
extractive stripper
solvent
Raffinate
solvent
solvent
hydrocarbons
recycled hydrocarbons
extractor
charge (aliphatic - aromatic stream)

Figure B-4 Separation of Benzene from Catalytic Reformate by the Sulfolane Process (Kirk-Othmer, 1976)

Table B-3 Sources of Benzene Releases Due to the Reformation Process

Source	Description of Release	Quantity of Benzene	Frequency	Points of Environmental Releases
I Catalyst:				
A. Regeneration 1. In situ	Coke that is formed on the catalyst is combusted. The resulting products CO_2, H_2O and some volatile hydrocarbons are stripped from the reformer by inert gas or steam.	Vapor concentrations are estimated in the ppm range.	The regeneration process can occur continuously or at least once a year per reformer. Depends on process severity.	Steam condensates go to the effluent treatment facility. Inert gas can go to one of four places: Vapor recovery process Flare Stock Vent
2. Replacement	The catalyst is shipped back to the vendor for reconditioning. Process unknown for reconditioning.	Vapor concentrations are estimated to be in the ppm range.	At least once a year per reformer.	During shipping and vendors location.
B. Replacement of spent catalyst	The spent catalyst and matrix-silica or alumina are returned to vendor. Vendor reclaims the noble metals. The recaptured noble metal is probably used in the production of new catalyst and matrix.	Vapor concentrations are estimated to be in the ppm range.	Estimated to be every 12 years but depends on process severity.	During shipping and vendors location.

Table B-3Sources of Benzene Releases Due to the Reformation Process (continued)

Source	Description of Release	Quantity of Benzene	Frequency	Points of Environmental Releases
II Hydrogen	The hydrogen gas from the reformer is regenerated and then recycled to the reformer.	Vapor concentrations are estimated to be greater than ppm range.	The hydrogen is probably regenerated and recycled after every run.	The vapors extracted during the recovery process are probably disposed of by one of the following methods: Vapor recovery process Flare Stack Vent
III Light gases collected at the separator	After the benzene stream leaves the reformer and as it enters the separator the light gases from the stream are taken off.	Vapor concentrations could possibly be in the pp thousand range.	At the end of every reforming process.	Represent a contaminant of the light gases. Benzene vapors released at the users site of the light gases.

Table B-4 Solvents Commercially Used in the Liquid-Liquid Aromatic Extraction Process[1]

Liquid-Liquid Extraction Process	Solvent Used	Extraction Conditions	
		Temperature	Pressure
Sulfolane[2]	Tetrahydrothiophene dioxide	50^oC	Atmospheric
Udex[2]	mono-, di-,tri-or tetraethyleneglycol water and mixtures of these	130^o-150^oC	5-7 bar
Aromex	N-Formylmorpholine	80^oC	2 bar
Arosolvan	N-Methylpyrrolidone/H_2O	20-40^oC	1 bar
Duo-Sol	Propane/cresol or phenol	unknown	unknown
Formex	N-Formylmorpholine	40^oC	1 bar
IFP	Dimethylsulfoxide/H_2O	20-30^oC	Atmospheric
Mofex	Monomethylformamide/H_2O	20-30^oC	0.1-0.4 bar
USSR	Propylene carbonate	20-50^oC	Atmospheric

1. The information contained in the table was adapted from Industrial Organic Chemistry by Klaus Weissermel and Hans-Jurgen Arpe.
2. Industry contacts indicated that Sulfolane and Udex processes are the most frequently used liquid-liquid extraction processes.

Table B-5 Sources of Benzene Releases Due to the Separation Process

Source	Description of Release	Quantity of Benzene	Frequency	Points of Environmental Releases
I Solvent A. Regeneration	The used separator solvent is put through an extractor unit which extracts the non-solvent material. The aromatics are recycled through the separator. The other organics may be recycled through the reformer or added to the raffinate.	0 to .7% of the benzene available for extraction.	After every run of benzene.	Follows the path of raffinate.
B. Spent Solvent	The spent solvent is reconstituted in the extractor. Any nonsolvent material follows the course stated above in regeneration. Rarely is the spent solvent disposed of.	It is estimated to be 0 to .7% of the benzene available for extraction.	Unknown Rarely	Follows the path of raffinate. Unknown
II Raffinate A. Raffinate	That part of the reformate that is not absorbed by the solvent. The raffinate after washing is sent to be blended into: gasoline; aviation gas or jet fuel; feed stock for olefin production.	It is estimated to be 0 to .1% of the available benzene for extraction.	After every run of benzene.	Sites of gasoline, aviation gas and jet fuel and olefin production.

Table B-5 Sources of Benzene Due to the Separation Process (continued)

Source	Description of Release	Quantity of Benzene	Frequency	Points of Environmental Releases
B. Raffinate Wash water	The raffinate is washed to remove solvent and any aromatics. The solvent and aromatics are reclaimed in recovery units. They are both recycled to their respective process entry points.	Up to the solubility in water, 0.7g/1	For every run of reformate sent to the extractor.	Wash water is sent to the refinery effluent treatment process. Benzene either collects in sludge or is emitted with the effluent.

Appendix B-5 Toluene Dealkylation

Table B-6 Toluene Hydrodealkylation Methods Used to Produce Benzene

Method[1]	Proprietary Process[1] Types	Method Conditions[2]	Yield	Environmental[2] Releases Peculiar to each method
Catalytic	Hydeal Detol Bextol[2]	Temperature 550° - 650°C; Pressure 30 - 50 bar Catalyst Cr; Mo; Co oxide on alumina supports	70 to 85% per pass with ultimate yields of 95-98%	Coking occurs and needs to be burned off every 2,000 - 4,000 hrs.
Thermal	HDA THD MHA[2]	Temperature 550° - 880°C Pressure 30 - 100 bar	60 - 90% per pass with ultimate yields of 95%	
Steam	New method in the development stages. No information was available.			

Footnotes:

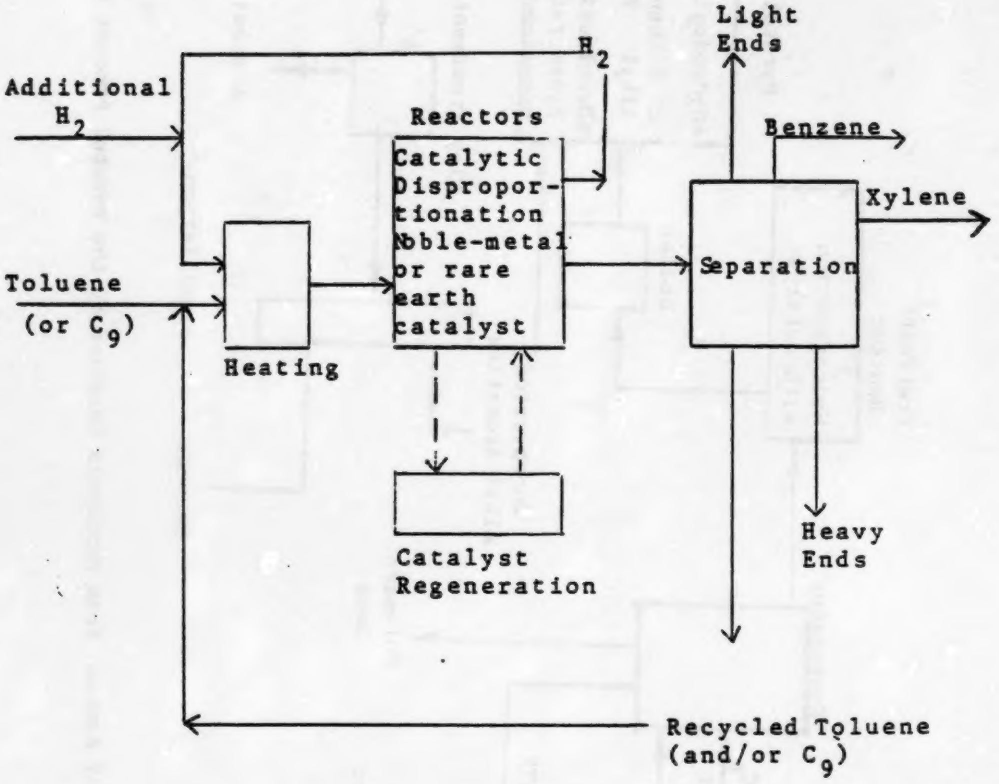
1. Kirk-Othmer 1976
2. Weissermel and Arpe 1978

Table B-7 Disproportionation and Transalkylation Processes for Benzene Production

Proprietary Process Names[1]	Users[1]	Process Description[1,3]	Yield[2,3]
Xylenes-plus	ARCO	Tatoray: 1. Feedstock of toluene or C_9 aromatics 2. Liquid feed with hydrogen to reduce coking is disproportionated catalytically with a rare-earth or noble-metal. 3. Reacting environment: 350°C to 530°C and a 5/12 to 1 hydrogen feed pressure 10-50 bar. 4. Distillative separation into a. toluene and C_9 aromatics b. reaction products benzene and xylene 5. Product - consists of every pure benzene and xylenes with the unreacted feedstock recycled	Their mole ratios determine the ratio of benzene to xylenes.
LTD	Mobile		
Tatoray	Unknown		

1. Kirk-Othmer 1976
2. SRI 1977
3. Weissermel and Arpe 1978

Appendix B-6 (continued)



Light Ends
H_2
Additional H_2
Reactors
Benzene
Catalytic Dispropor-tionation Noble-metal or rare earth catalyst
Xylene
Toluene (or C_9)
Separation
Heating
Catalyst Regeneration
Heavy Ends
Recycled Toluene (and/or C_9)

Figure B-5 Toluene Disproportionation by the Tatoray Process (adaptation from Kirk-Othmer 1976)

Appendix B-7 Benzene from Pyrolysis Gasoline

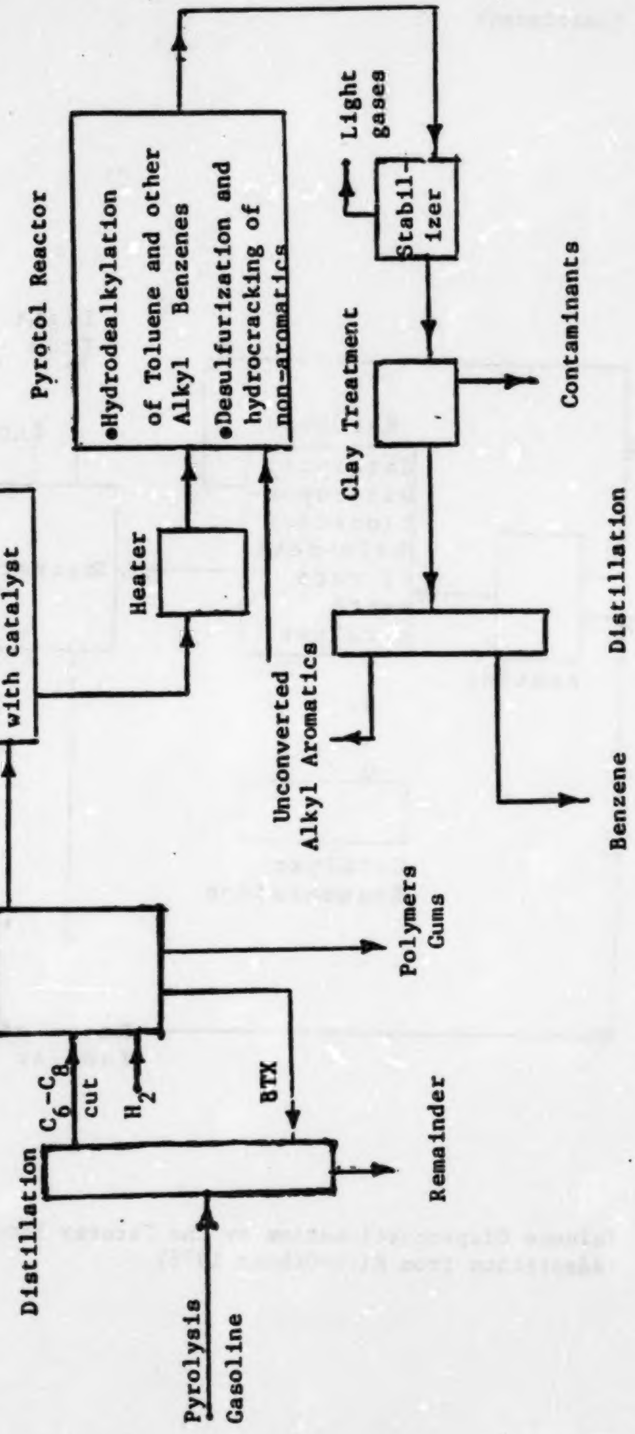

Pyrolysis Gasoline
Distillation
C_6-C_8 cut
H_2
BTX
Remainder
Evaporator
Polymers Gums
Pretreat Reactor
Hydrogenation with catalyst
Heater
Unconverted Alkyl Aromatics
Pyrotol Reactor
•Hydrodealkylation of Toluene and other Alkyl Benzenes
•Desulfurization and hydrocracking of non-aromatics
Light gases
Stabilizer
Clay Treatment
Contaminants
Distillation
Benzene

Figure B-6 Recovery of Benzene from Pyrolysis Gasoline by the Pyrotol Process (Kirk-Othmer 1976)

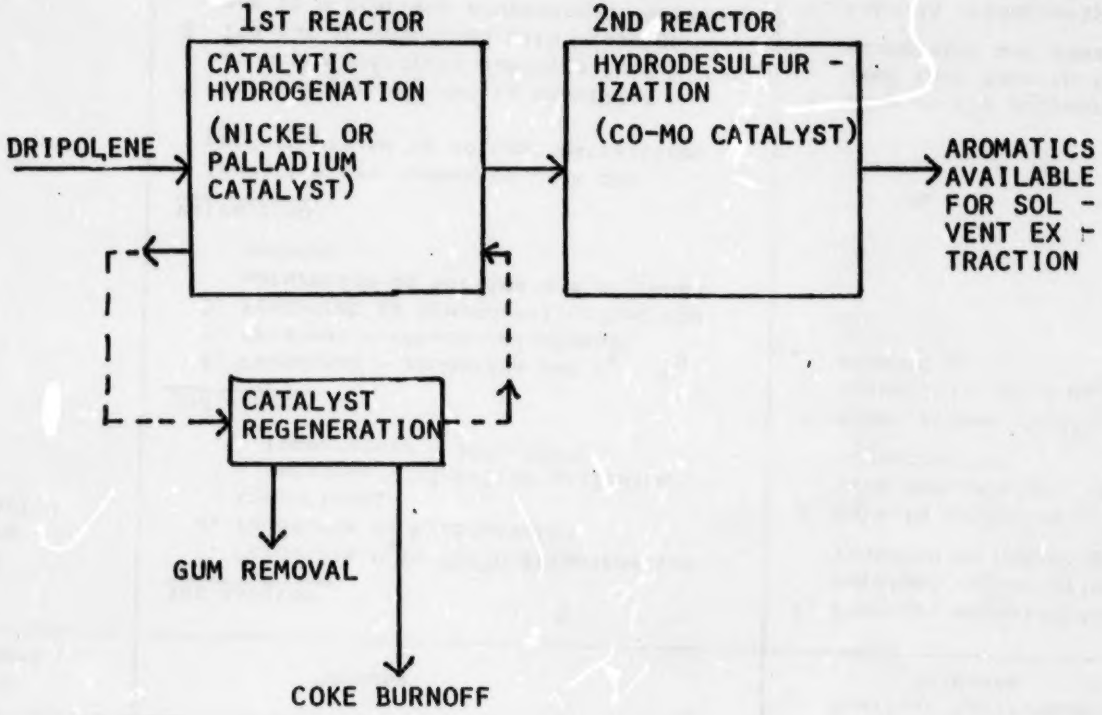

1ST REACTOR
CATALYTIC HYDROGENATION
(NICKEL OR PALLADIUM CATALYST)
2ND REACTOR
HYDRODESULFUR - IZATION
(CO-MO CATALYST)
DRIPOLENE
AROMATICS AVAILABLE FOR SOL - VENT EX - TRACTION
CATALYST REGENERATION
GUM REMOVAL
COKE BURNOFF

Figure B-7 Recovery of Benzene from Pyrolysis Gasoline (Dripolene) by the IFP (Institute Francaise de Petrole) Process: After Kirk-Othmer 1976

Table B-8 Pyrolysis Gasoline Processes and Types of Releases[1]

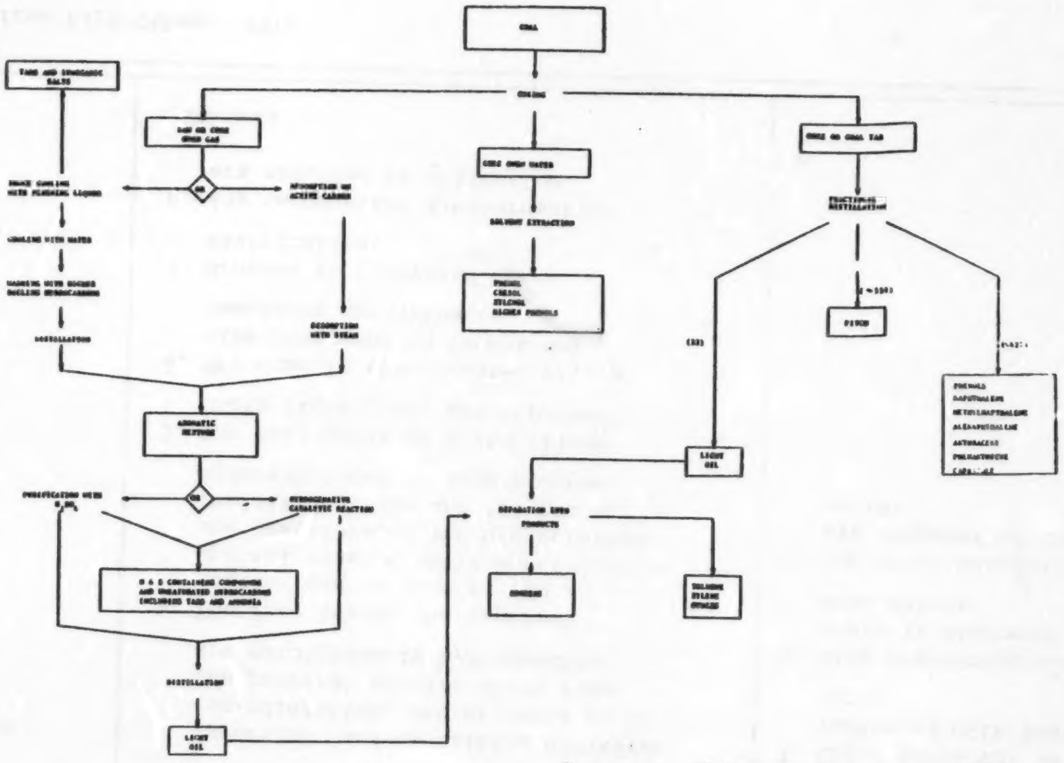
Proprietary Process Names	Process	Possible Environmental Releases
IFP (pyrolysis distillate hydrogenation process)	1st Reactor 1. Feedstock C_9 to 205°C dripolene cut 2. Feedstock is hydrogenated 3. Conditions; catalyst - nickel or palladium temperature - 75°C-150°C 2nd Reactor 1. Feedstock - aromatics cut C_6 - C_8 2. Catalyst - cobalt-molybdenum 3. Feedstock is hydrodesulfurized and saturation of olefins and styrenes occurs. Extraction Aromatics are recovered from the product stream by solvent extraction.	1. Frequent nonoxidative catalyst regeneration required to remove gums. 2. Coke is oxidatively removed from the catalyst during regeneration. 3. Under proper conditions essentially no loss of aromatics.
Pyrotol	1. Feedstock-C_9-C_8 cut is distilled from the pyrolysis gasoline feed 2. The cut is vaporized with hydrogen gas in a pretreat evaporator. These are recycled back to the feed distillation column.	1. Some of the polymers and gums that form in the evaporator may remain. 2. Coke is oxidatively removed from the catalyst during regeneration.

Table B-8 Pyrolysis Gasoline Processes and Types of Releases[1] (continued)

Proprietary Process Names	Process	Possible Environmental Releases
Continuation of the Pyrotol Process	3. Vaporized feed containing diolefins, cyclodiolefins, and styrenes go to the pretreat reactor where they are catalytically hydrogenated. 4. The feed leaves the pretreat reactor and is sent to the pyrotol reactor where nonaromatics are desulfurized and hydrocracked. The alkybenzenes and toluene are hydroalkylated to form benzene. 5. The feed moves to a stabilizer where light gases are separated. 6. The feed is then treated with a clay treatment to remove any remaining contaminants. 7. Benzene is recovered by distillation. 8. Any unconverted alkylaromatics are recycled to extinction.	3. Light gases may be contaminated with benzene vapor. 4. Clay containing contaminants is disposed of in some matter. 5. Converted alkylaromatics are disposed of in some matter.
DPO	Unknown	

[1] Adapted from Kirk-Othmer 1976

Appendix B-8 Coal Processing


COAL
COKING
TARS AND INORGANIC SALTS
GAS OR COKE OVEN GAS
COKE OVEN WATER
COKE OR COAL TAR
OR
DEEP COOLING WITH FLUSHING LIQUOR
ADSORPTION ON ACTIVE CARBON
SOLVENT EXTRACTION
PHENOL
CRESOL
XYLENOL
HIGHER PHENOLS
FRACTIONAL DISTILLATION
COOLING WITH WATER
WASHING WITH HIGHER BOILING HYDROCARBONS
DISTILLATION
DESORPTION WITH STEAM
PITCH
PHENOLS
NAPHTHALENE
METHYLNAPHTHALENE
ALKYLNAPHTHALENE
ANTHRACENE
PHENANTHRENE
CARBAZOLE
AROMATIC MIXTURE
LIGHT OIL
OR
PURIFICATION WITH H_2SO_4
HYDROGENATIVE CATALYTIC REACTION
SEPARATION INTO PRODUCTS
N & S CONTAINING COMPOUNDS AND UNSATURATED HYDROCARBONS INCLUDING TARS AND AMMONIA
BENZENE
TOLUENE
XYLENE
OTHERS
DISTILLATION
LIGHT OIL

Sources: Weissermal & Arpe, 1978; A.D. Little, 1977

Figure B-8 Flow Diagram for Coal Processing

Appendix B-9 Ethylbenzene Production

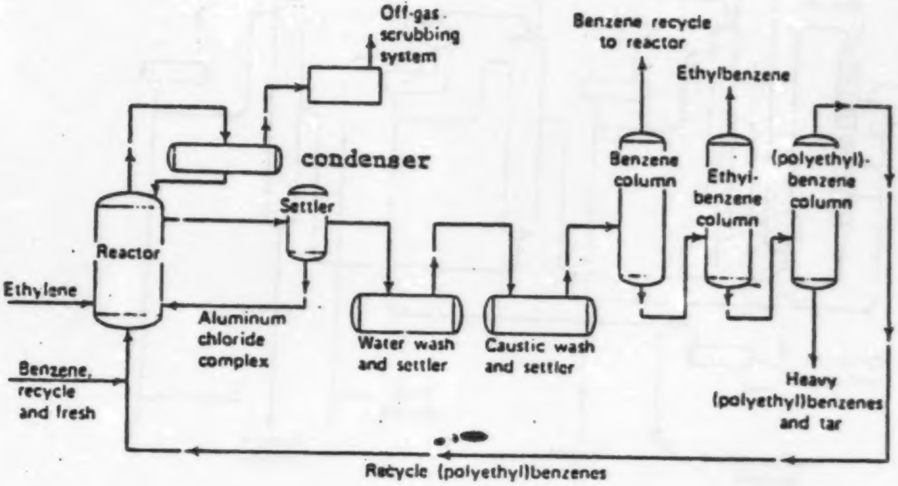

Off-gas scrubbing system
Benzene recycle to reactor
Ethylbenzene
condenser
Settler
Benzene column
Ethyl-benzene column
(polyethyl)-benzene column
Reactor
Ethylene
Aluminum chloride complex
Water wash and settler
Caustic wash and settler
Benzene, recycle and fresh
Heavy (polyethyl)benzenes and tar
Recycle (polyethyl)benzenes

Figure B-9 The Manufacture of Ethylbenzene Employing Aluminum Chloride as Catalyst

Appendix B-10 Cumene Production

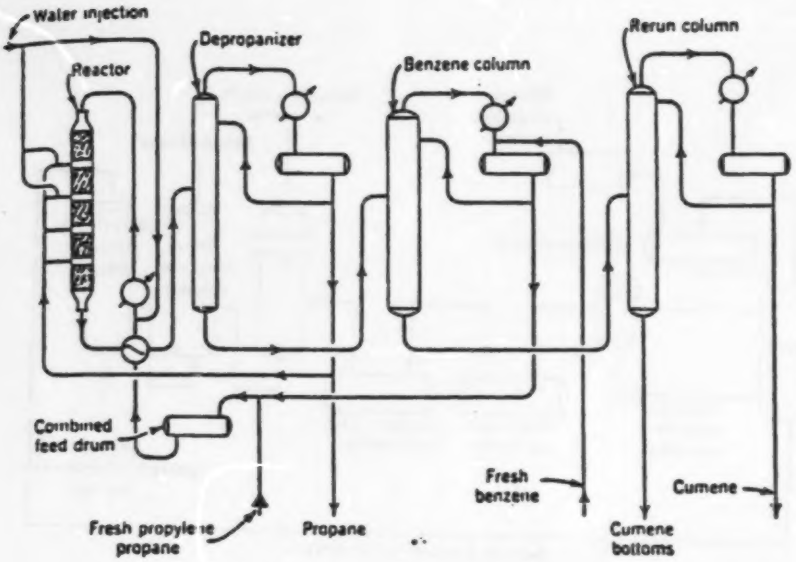

Water injection
Reactor
Depropanizer
Benzene column
Rerun column
Combined feed drum
Fresh propylene propane
Propane
Fresh benzene
Cumene bottoms
Cumene

Figure B-10 Solid Phosphoric Acid Process for Cumene Production
(Source: A.D. Little, Inc. 1977)

Appendix B-11 Cyclohexane Production

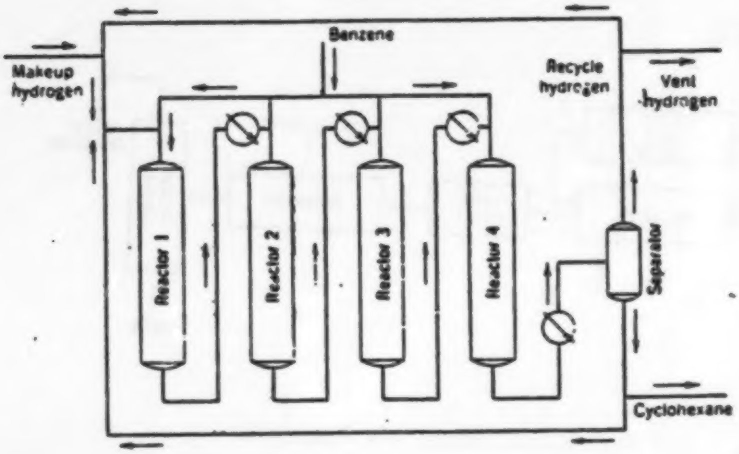

Benzene
Makeup hydrogen
Recycle hydrogen
Vent hydrogen
Reactor 1
Reactor 2
Reactor 3
Reactor 4
Separator
Cyclohexane

Figure B-11 Hydrogenation of Benzene

Appendix B-12 Maleic Anhydride Production

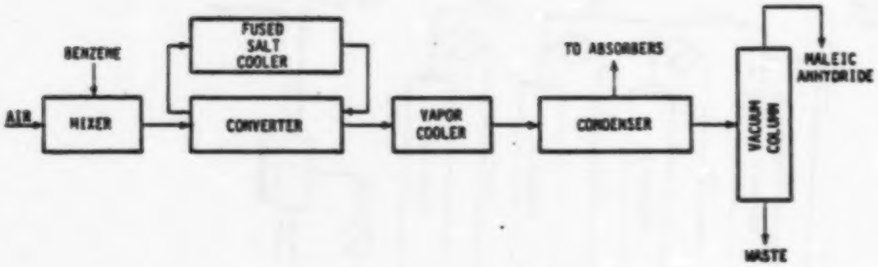

BENZENE
AIR
MIXER
FUSED SALT COOLER
CONVERTER
VAPOR COOLER
TO ABSORBERS
CONDENSER
VACUUM COLUMN
MALEIC ANHYDRIDE
WASTE

Figure B-12 Flow Chart for Maleic Anhydride Synthesis

Appendix B-13 Nitrobenzene Production

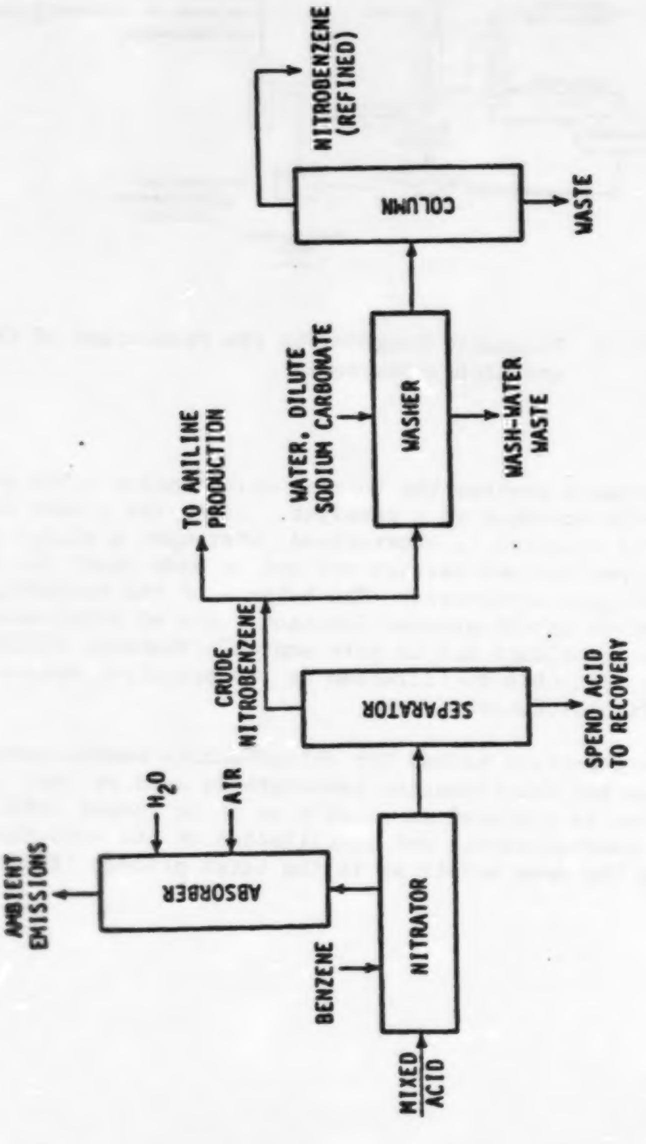

MIXED ACID
BENZENE
NITRATOR
ABSORBER
AMBIENT EMISSIONS
H2O
AIR
SEPARATOR
SPEND ACID TO RECOVERY
CRUDE NITROBENZENE
TO ANILINE PRODUCTION
WATER, DILUTE SODIUM CARBONATE
WASHER
WASH-WATER WASTE
COLUMN
WASTE
NITROBENZENE (REFINED)

Figure B-13 Process Flow for Nitrobenzene Synthesis

Appendix B-14 Chlorobenzenes Production

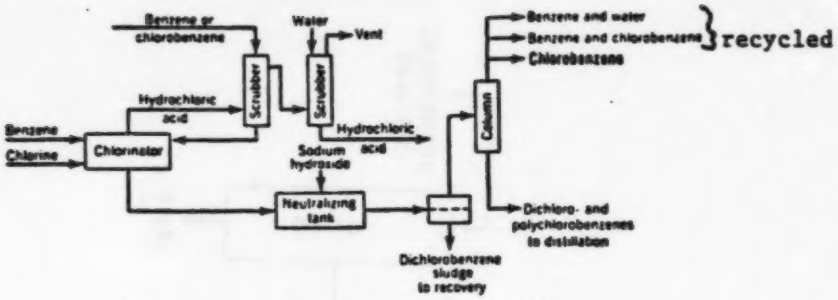

Benzene or chlorobenzene
Water
Vent
Scrubber
Scrubber
Benzene and water
Benzene and chlorobenzene
recycled
Chlorobenzene
Hydrochloric acid
Column
Benzene
Chlorine
Chlorinator
Hydrochloric acid
Sodium hydroxide
Neutralizing tank
Dichloro- and polychlorobenzenes to distillation
Dichlorobenzene sludge to recovery

Figure B-14 Schematic Diagram for the Production of Chlorobenzene and Dichlorobenzenes

In the batch process the benzene chlorination takes place at 40°C to 60°C in the presence of a catalyst. After the proper density is attained, the solution is neutralized, whereupon a sludge with a high dichlorobenzene content settles out and is made ready for recovery of the *ortho* and *para* structures. The balance of the neutralized solution is distilled to obtain several fractions, one of which contains 75 percent of the distillate and is pure monochlorobenzene (PEDCo, Inc. 1977). The residue from this distillation is the principal source of *para-* and *ortho*-dichlorobenzene.

In the alternate method for chlorobenzene manufacture a continuous chlorination and fractionation procedure is used so that the monochlorobenzene is isolated as quickly as it is formed (PEDCo 1977). At this point neutralization and distillation of the monochlorobenzene is executed in the same manner as in the batch process (PEDCo 1977).

Appendix B-15 Biphenyl Production

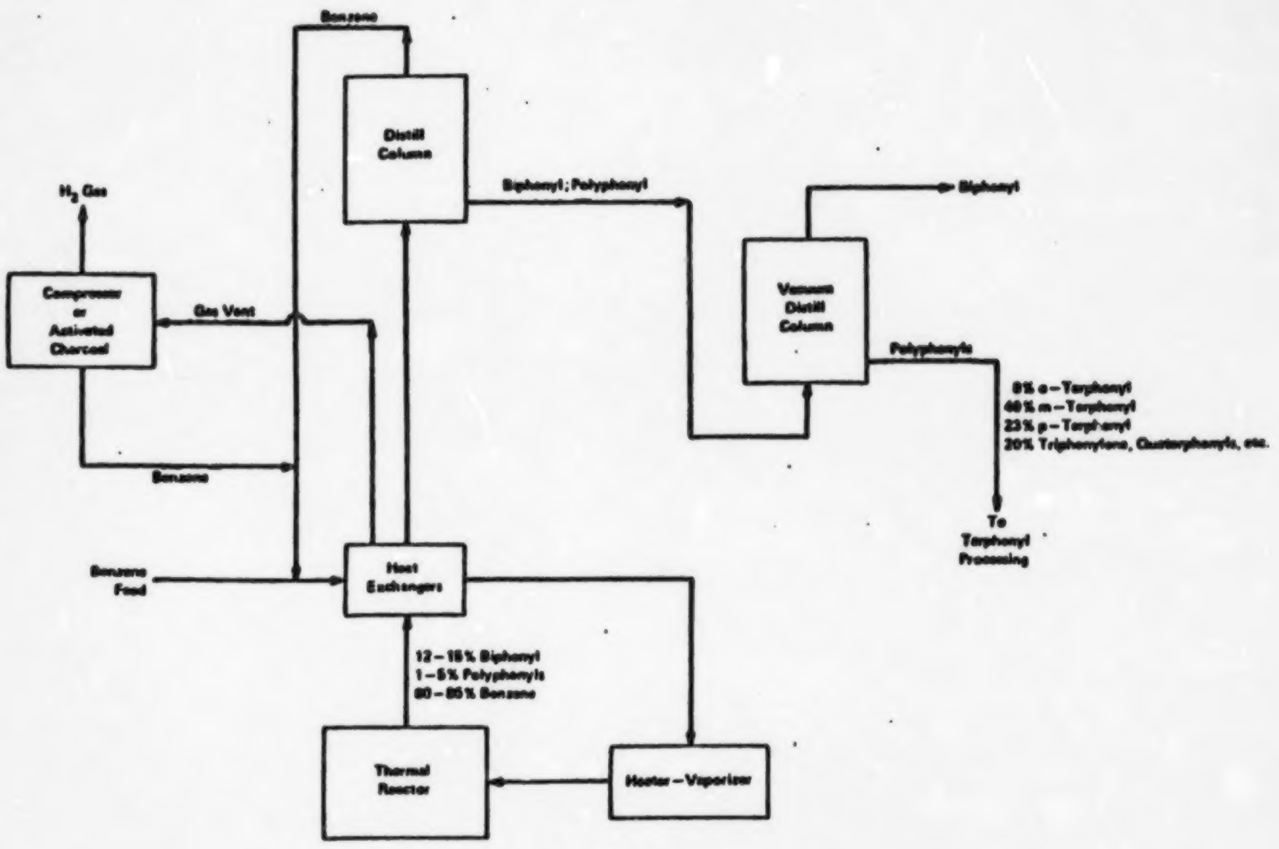

Benzene
Distill Column
H_2 Gas
Compressor or Activated Charcoal
Gas Vent
Biphenyl; Polyphenyl
Biphenyl
Vacuum Distill Column
Polyphenyls
8% o–Terphenyl
49% m–Terphenyl
23% p–Terphenyl
20% Triphenylene, Quaterphenyls, etc.
To Terphenyl Processing
Benzene
Benzene Feed
Heat Exchangers
12–15% Biphenyl
1–5% Polyphenyls
80–85% Benzene
Thermal Reactor
Heater–Vaporizer

Figure B-15 Biphenyl from Thermal Dehydrogenation of Benzene
(Source: Meylan and Howard 1976)

APPENDIX C

CALCULATIONS

C-1 Cumene Release Factor C-1

C-2 Cyclohexane Release Factor C-3

C-3 Nitrobenzene Release Factor C-5

C-4 Benzene in Consumer Product Solvents C-6

Appendix C-1Calculation of Benzene Release Factor (Uncontrolled) from Peterson (1979)

	Release Factor, kkg/kkg of Cumene			
	SPA Process (77%)		$AlCl_3$ Process (23%)	
Source	Uncontrolled	Controlled	Uncontrolled	Controlled
Process vents A_1	0	---	2×10^{-5}	1×10^{-6}
A_2	9.4×10^{-3}	9.4×10^{-5}	1.6×10^{-4}	1.6×10^{-5}
A_3	0	0	7.8×10^{-6}	3.9×10^{-7}
A_4	---	---	1.7×10^{-5}	8.5 x 10-7
Fugitive	---	---	---	---
Storage and handling	6.2×10^{-4}	7.7×10^{-5}	9.2×10^{-4}	9.6×10^{-5}
Secondary	---	---	---	---
Total	1.0×10^{-2}	1.7×10^{-4}	1.1×10^{-3}	1.1×10^{-4}

Representative release factors, based on 15 percent uncontrolled releases and 85 percent controlled releases, are calculated as follows:

$$\begin{pmatrix}\text{Percent}\\ \text{uncontrolled}\end{pmatrix}\begin{pmatrix}\text{Uncontrolled}\\ \text{Release Factor}\end{pmatrix} + \begin{pmatrix}\text{Percent}\\ \text{controlled}\end{pmatrix}\begin{pmatrix}\text{Controlled}\\ \text{release}\\ \text{factor}\end{pmatrix} = \begin{matrix}\text{Release}\\ \text{factor}\\ \text{per kkg}\\ \text{of}\\ \text{cumene}\end{matrix}$$

SPA process:

$$(0.15)(1.0 \times 10^{-2}) + (0.85)(1.7 \times 10^{-4}) = 1.6 \times 10^{-3}$$

$AlCl_3$ process:

$$(0.15)(1.1 \times 10^{-3}) + (0.85)(1.1 \times 10^{-4}) = 2.6 \times 10^{-4}$$

Appendix C-1 (continued)

A weighted average is calculated by assuming that 77 percent of production is by SPA process; 23 percent, by $AlCl_3$ process.

$$\begin{pmatrix}\text{Fraction}\\ \text{by SPA}\\ \text{process}\end{pmatrix}\begin{pmatrix}\text{SPA release}\\ \text{per kkg of}\\ \text{cumene}\end{pmatrix} + \begin{pmatrix}\text{Fraction}\\ \text{by } AlCl_3\\ \text{process}\end{pmatrix}\begin{pmatrix}AlCl_3 \text{ release}\\ \text{per kkg}\\ \text{of cumene}\end{pmatrix} = \begin{matrix}\text{Weighted}\\ \text{release}\\ \text{factor}\\ \text{per kkg}\\ \text{of cumene}\end{matrix}$$

$$(0.77)(1.6 \times 10^{-3}) \quad + \quad (0.23)(2.6 \times 10^{-4}) \quad = 1.3 \times 10^{-3}$$

This factor is expressed in terms of benzene used by the following conclusions.

$$\begin{pmatrix}\text{Release factor}\\ \text{per kkg of}\\ \text{cumene}\end{pmatrix} \div \begin{pmatrix}\text{Benzene used}\\ \text{per kkg of}\\ \text{cumene produced}\end{pmatrix} = \begin{matrix}\text{Release factor}\\ \text{per kkg of}\\ \text{benzene used}\end{matrix}$$

$$(1.3 \times 10^{-3}) \quad \div \quad (0.67) \quad = \quad 1.9 \times 10^{-3}$$

Appendix C-2 Calculation of Benzene Release Factor Due to Cyclohexane Synthesis from the Data of Blackburn (1978)

This estimate of the release factor was based on estimates of releases from three model plants with cyclohexane capacities of 50,000 kkg, 150,000 kkg, and 250,000 kkg/yr. These steps in the calculation are as follows:

I. Weighting factors for model plants.

Because the model plants have different release characteristics, it was necessary to represent each operating plant by the model plant with the closest capacity. This was done for the 10 plants listed in Blackburn (1978).

The 50 x 10^3 kkg/yr model plant applied to 4 plants with combined capacities of 276 x 10^3 kkg/yr (23 percent of total capacity).

The 150 x 10^3 kkg/yr model plant applied to 5 plants with combined capacities of 642 x 10^3 kkg/yr (54 percent of total capacity).

The 250 x 10^3 kkg/yr model plant applied to one plant with a capacity of 265 x 10^3 kkg/yr (22 percent of total capacity).

II. Weighted average annual releases, uncontrolled.

The uncontrolled release rates for the three model plants were estimated to be 4.17 kg/hr for the 50,000 kkg/yr plant, 10.96 kg/hr for the 150,000 kkg/yr plant, and 17.93 kg/hr for the 250,000 kkg/yr plant. A weighted average of the uncontrolled benzene release rates for the three model plants was:

$$(0.23)(4.17 \text{ kg/hr}) + (0.54)(10.96 \text{ kg/hr}) + (0.22)(17.93 \text{ kg/hr}) = 10.8 \text{ kg/hr}$$

Annual releases were:

$$(10.8 \text{ kg/hr})(8{,}760 \text{ hr/yr}) = 9.46 \times 10^4 = 94.6 \text{ kkg/yr.}$$

III. Weighted average annual releases, controlled.

Similarly, a weighted average of the controlled benzene release rates for the three model plants was calculated from the respective estimated release rates:

$$(0.23)(0.16 \text{ kg/hr}) + (0.54)(0.32 \text{ kg/hr}) + (0.22)(0.44 \text{ kg/hr}) = 0.31 \text{ kg/hr}$$

Annual releases were:

$$(0.31 \text{ kg/hr})(8{,}760 \text{ hr/yr}) = 2.7 \times 10^3 \text{ kg/yr} = 2.7 \text{ kkg/yr.}$$

IV. Composite annual release assuming 50 percent control.

$$\frac{94.6 \text{ kkg/yr} + 2.7 \text{ kkg/yr}}{2} = 49 \text{ kkg/yr}$$

V. Weighted average annual production by model plants.

In order to derive a release factor applicable to production instead of capacity, it was assumed that the model plants were operating at 100 percent capacity.

$$(0.23)(50 \times 10^3 \text{ kkg/yr}) + (0.54)(150 \times 10^3 \text{ kkg/yr}) +$$
$$(0.22)(250 \times 10^3 \text{ kkg/yr}) = 150 \times 10^3 \text{ kkg/yr}$$

VI. Composite release factor.

$$\frac{49 \text{ kkg/yr}}{150 \times 10^3 \text{ kkg/yr}} = 3.2 \times 10^{-4} \frac{\text{kkg}}{\text{kkg product}}$$

Appendix C-3 Calculation of Benzene Release Factor Due to Nitrobenzene Synthesis (Hobbs and Stuewe 1979)

I. Weighting factors for model plants.

The 30 x 10^9 g/yr model plant applied to five plants with 1977 capacities of 24.9, 38.5, 27.2, 4.5, and 34 x 10^9 g/yr. This total capacity, 129 x 10^9 g/yr, was 24 percent of 1977 estimated capacity. The 90 x 10^9 g/yr model plant applied to two plants with 1977 capacities of 90.7 and 61.2 x 10^9 g/yr. This total capacity, 152 x 10^9 g/yr, was 28 percent of 1977 estimated capacity.

The 150 x 10^9 model year plant applied to two plants with 1977 capacity of 140.6 and 122.4 x 10^9 g/yr. This total capacity, 263 x 10^9 g/yr, was 48 percent of 1977 estimated capacity.

II. Weighted average annual releases, uncontrolled.

A weighted average of the uncontrolled benzene release rates for the three model plants was:

$$(0.24)(10.8 \text{ kg/hr}) + (0.28)(24.5 \text{ kg/hr}) + (0.48)(38.0 \text{ kg/hr}) = 28 \text{ kg/hr}$$

Annual releases for an 8,760-hour year were:

$$(28 \text{ kg/hr})(8{,}760 \text{ hr/yr}) = 2.5 \times 10^5 \text{ kg/yr.}$$

III. Weighted average annual releases, controlled.

A weighted average of the controlled benzene release rates for the three model plants was:

$$(0.24)(0.83 \text{ kg/hr}) + (0.28)(1.69 \text{ kg/hr}) + (0.48)(2.53 \text{ kg/hr}) = 1.9 \text{ kg/hr}$$

Annual releases for an 8,760-hour year were:

$$(1.9 \text{ kg/hr})(8{,}760 \text{ hr/yr}) = 1.7 \times 10^4 \text{ kg/hr}$$

IV. Composite annual release using Hydroscience estimate of 50 percent industry controls:

$$\frac{2.5 \times 10^5 \text{ kg/yr} + 1.7 \times 10^4 \text{ kg/yr}}{2} = 1.3 \times 10^5 \text{ kg/yr}$$

V. Weighted average annual production by model plants.

$$(0.24)(30 \times 10^9 \text{ g/yr}) + (0.28)(90 \times 10^9 \text{ g/yr}) +$$
$$(0.48)(150 \times 10^9 \text{ g/yr}) = 100 \times 10^9 \text{ g/yr}$$

VI. Composite release factor.

$$\frac{1.3 \times 10^8 \text{ g/yr released}}{1.0 \times 10^{11} \text{ g/yr produced}} = 1.3 \times 10^{-3} \text{ kkg/kkg of product}$$

APPENDIX C-4 CALCULATION OF BENZENE AMOUNTS IN CONSUMER PRODUCTS SOLVENTS

(Source: Hillman et al. 1978)

Solvent	Amount Used, 1977 (10^6 gal)	Avg. Maximum Benzene[1] (% by volume)	Range[2]	Benzene Present (10^6 gal)	(kkg)
Toluene	9	0.2	0.0005 - 0.5	0.02	70
Hexane	1.3	0.08	0 - 0.2	0.001	3
Heptane	0.4	0.08	0.01 - 0.1	0.0003	1
Rubber solvent	8	0.4	0.01 - 1.8	0.03	10
Lacquer diluent	0.5	0.1	0 - 0.5	0.0005	2
Xylene	7	0.1		0.007	20
VM&P naphtha	2	0.1		0.002	7
Mineral spirits	90	0.03		0.03	10
Kerosene	5	0.01		0.0005	2
					125

1. The average of the upper end of the benzene concentration ranges.
2. Available only for the five benzene-critical solvents (those in which benzene concentration sometimes exceeds 0.1 percent by volume).